A STUDY OF THE LONG TERM FATE AND BEHAVIOUR OF HEAVY OILS

by

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ACKNOWLEDGEMENTS

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1.0 INTRODUCTION

Numerous experimental studies and observations of real spill behaviour have shown that when conventional and heavy crude oils and petroleum products are spilled in the marine environment they are subject to a number of processes collectively termed "weathering", which cause profound changes in the oils' physical and chemical properties and composition. As weathering proceeds, the oils usually become denser, and their viscosity increases, and ultimately the oil masses may form semi-solid droplets or tar balls which float in a near-submerged state at the water surface. This material may persist indefinitely on the sea surface, or become stranded on shore, or sink and become incorporated into sediments. It is important to determine which types of oils, under which conditions, are subject to which type of behaviour. Whereas most experimental measurements are being made over the short-term, it is increasingly obvious that there is a need to predict long term behaviour of oil because this oil may drift appreciable distances from the source of the spill.

The purpose of this study is to design and test various methods which can yield quantitative data for the long-term weathering phenomena of crude oils, especially heavy crude oils, thereby, establishing an experimental protocol. Ultimately, it is desirable to develop some form of mathematical modelling approach to translate laboratory results to marine environmental conditions.

The experimental approach taken was first to quantify evaporation and dissolution on an individual basis. Evaporation is of importance because it can cause appreciable density and viscosity increases. One aim is to devise an experimental protocol for measuring the extent to which hydrocarbons will evaporate from oil, and in doing so, identify the hydrocarbons which have evaporated. This is done in the hope that the protocol may be useful for routine characterization of oils in the marine or aquatic environment.

Dissolution is less important from the viewpoint of loss of mass by the oil, but it is critically important for the assessment of toxicity to aquatic and marine organisms. Again, the objective is to develop an experimental protocol whereby oils may be subjected to controlled dissolution conditions, and the dissolved and remaining oil identified and quantified.

A second aspect has been to devise a relatively simple laboratory system for measuring and observing the long-term weathering of crude oils on a water surface. The oil is thus subjected to evaporation and dissolution simultaneously.

Any attempt to prepare a mathematical model of oil behaviour is rendered difficult because of the very complex nature of crude oils, especially the large number of components which are of unknown structure and properties. In this study, an attempt has been made to develop a novel "matrix" approach for oil characterization during long-term weathering by modifying a procedure developed for characterizing the long-term weathering behaviour of oils in a soil environment (Eastcott et al., 1990). The general concept is that the oil is divided up into a number of pseudocomponents or elements, each of which has defined properties such as volatility, solubility, density, and viscosity. As the oil is weathered, there is selective removal of these pseudocomponents caused by exposure to evaporation or dissolution. The result is a change in the proportion of the chemicals present in the matrix, and thus a change in the properties of the bulk oil. In principle, it should be possible to characterize the changing properties of the bulk oil from the properties and changes in the magnitude of the matrix elements.

The key problem is the development of analytical techniques which will enable the hydrocarbons in the original and weathered oils to be categorized in a two-dimensional matrix. Gas chromatography is very convenient as a method of characterizing the volatility of crude oils; thus one dimension of the matrix should obviously be a separation of oil into rows which consist of pseudocomponents or

elements similar in volatility. It is desirable to separate the oil into matrix columns based on solubility, but this is more difficult. A first approach is to divide up the oil into classes of hydrocarbons such as alkanes, aromatics and polars which are known to have widely different solubility characteristics. This is done experimentally by open column chromatographic separation. A second approach is to separate the oil into groups of hydrocarbons which have similar solubilities. The different matrix approaches are investigated with the viewpoint of determining the preferred one. A synthetic oil is valuable for testing and validating the models because it is a simple hydrocarbon mixture with known amounts of compounds and well-established properties. A model which can be validated using the synthetic oil can be applied with more confidence to heavy crude oils.

In summary, the objectives of this study are

• to devise protocols for exposing crude oils to evaporation and dissolution in isolation under controlled conditions,

• to suggest and test analytical methods which can be used to determine the composition changes resulting from evaporation and dissolution,

• to devise and test a system which exposes oil to both processes simultaneously for a relatively long period (months) under conditions similar to those existing on an ocean surface, and

• to attempt to model the effect of these processes on oil composition with a view to estimating other oil properties such as density and viscosity.

2.0 LITERATURE BACKGROUND

2.1 Weathering Processes

Reviews which assessed the present understanding of the weathering processes have been compiled by Jordan and Payne (1980), Huang (1983), Mackay (1987), Mackay and McAuliffe (1988), Lee et al. (1989), and in the National Academy of Sciences reviews (1975, 1985). Recent research is reported in the biennial American Petroleum Institute Oil Spill Conference proceedings, and in the proceedings of the Environment Canada Arctic Marine Oilspill Technical Seminars. The most understood weathering phenomena are evaporation and dissolution. It is with some confidence that descriptive equations can been developed for these two processes.

2.1.1 Evaporation

Many studies under laboratory and field conditions have been conducted to investigate the effects of evaporation and dissolution on the behaviour of crude oils. Evaporation is an important weathering process in that it is the major mechanism which alters the oil mass and composition, and thereby, causes substantial changes in the oil's physical and chemical properties such as density and viscosity. It tends to remove the more volatile hydrocarbons from the oil most rapidly, that is, 50-70% of volatile lower molecular weight compounds are evaporated in 10 to 20 hours after an oil spill. Expressions which quantify the evaporation rate have been developed by Yang and Wang (1977), Reijhart and Rose (1982), Mackay et al. (1980) and Stiver and Mackay (1984) using the mass transfer approach.

Stiver and Mackay (1984) introduced the concept of a dimensionless evaporative

exposure, which is denoted as Q_E, for the characterization of environmental and laboratory exposure conditions. It is defined as

$$Q_E = \frac{KAt}{V_O}$$ [2.1]

where A is the spill area (m²), V_O is the initial volume of oil (m³), K is the overall mass transfer coefficient (m/s) and t is the time of exposure (s). The evaporative exposure Q_E can also be viewed as the ratio of exposed vapour volume to the initial liquid volume. It provides a basis for comparing evaporation rates under a variety of environmental conditions. This is done by combining the exposure Q_E with physical-chemical properties of the oil, namely the dimensionless air-to-oil partition coefficient of the chemical species H_E. As shown later, it is the group $H_E Q_E$ which controls the extent of evaporation. A similar approach can be applied to the dissolution process invoking an exposure term Q_D and the water-to-oil partition coefficient H_D.

2.1.2 Dissolution

Dissolution is primarily of concern from a toxicological viewpoint to the aquatic and marine organisms. It is not important from the viewpoint of mass depleted from the bulk oil, since less than 1% of the total mass is removed by dissolution. Harrison et al. (1975) have examined rates of disappearance of aromatic and aliphatic compounds from small surface slicks. It was found that dissolution rates are less than half of evaporation rates for these compounds. However, it has been shown that the dissolved hydrocarbons are relatively short-lived in the water column because they are still susceptible to

evaporation. Hamoda et al. (1989) carried out studies on the volatilization of the portion of crude oil dissolved in water. After 12 hours, approximately 80-95% of the dissolved hydrocarbons have been removed from solution by evaporation.

2.1.3 Water-in-Oil Emulsion Formation and Photolysis

Previous reviews of the formation of water-in-oil emulsions or "mousses" have been presented by Payne and Phillip (1985) and Mackay (1987). These emulsions are generally of high viscosity and high water content, and they profoundly affect oil behaviour and feasibility of clean-up. The susceptibility of oils to form stable emulsions was studied recently by Bobra (1990). It was found that asphaltenes, resins and waxes in finely divided particles are effective emulsifiers. The mechanisms of mousse formation are not well understood. There is presently no existing equation which gives an adequate description of this process.

Oil spilled in the marine environment is also subject to photolysis as a result of absorption of photons from sunlight. Sunlight has sufficient energy to cause the formation of free radicals which may cause oxidation, resulting in the formation of carboxylic acids, carbonyl compounds, alcohols, aldehydes, and other oxygenated compounds (Bongiovanni et al., 1989). Generally, these polar compounds are considerably more water soluble than the parent hydrocarbons, and the toxicity of the water-soluble fractions may increase in the water column. Photolysis also induces the formation of surface-active compounds which enhance the formation and stabilization of emulsions. There have been a few studies on the photolysis of crude oils by Lichtenthaler et al. (1988) and Bobra (1989). The present ability to write a descriptive

equation about the photolytic process is inadequate when compared to evaporation and dissolution.

2.2 Hydrocarbon Group-Type Separations and Analyses

Liquid chromatography has been used to provide detailed characterization of crude oils and petroleum products in the petroleum industry. It is used for the purposes of fingerprinting, hydrocarbon type analysis, and preparative separation into hydrocarbon classes.

Methods have been developed for separating these hydrocarbon products into class fractions such as saturates, olefins, aromatics and polars, or into aromatic ring-number fractions such as saturates, mono-, di-, tri-, and polyaromatics and polars because the complexity of crude oils often requires preparative separation prior to instrumental analyses. The compounds in each fraction can be identified by gas chromatography or a combination of gas chromatography and mass spectrometry. Suatoni and Swabi (1975), and Hayes and Anderson (1986) developed high performance liquid chromatographic (HPLC) methods to determine hydrocarbon group types of saturates, olefins, aromatics, polar compounds and asphaltenes. Matsunaga (1983) and Gizzle and Sablotny (1986) studied the separation of crude oils and related materials (Rashid et al., 1989) into aromatic-ring fractions by HPLC using several commercially available packings.

For quantitative work, calibration of the detector is necessary to establish its response factors. This is a major difficulty with the HPLC methods. Another problem is the selection of a calibration standard which will give the correct or rational detector response times. One approach is to obtain calibration standards from a crude oil which

has been separated into the various fractions by classical liquid chromatographic separation. Open column liquid chromatography on alumina-silica gel is described by Cook and Westlake (1976). This approach fractionates crude oils into saturates, aromatics and polar compounds. It is time-consuming if applied to routine analysis; however, it is useful as a hydrocarbon group separation method for a relatively small number of samples. Each of the methods must incorporate a sample preparation step to remove the asphaltenes from the oils prior to group-type separation. The individual fractions are quantified gravimetrically after the removal of the solvent used in the elution.

It is desirable to have a preparative or semi-preparative liquid chromatographic method which will provide fractions for better characterization of crude oils with other analytical techniques.

2.3 Mathematical Models

There are incentives to describe in quantitative terms the fate of oil spilled in the marine environment. A mathematical model would increase our understanding of petroleum fate, and improve remedial measures. However, it is difficult to predict the behaviour of crude oils in the marine environment because of the oils' complex nature. They consist of several thousands of compounds of which many have unknown structures and properties. Some researchers attempted to simplify the multicomponent oil system by dividing up its compounds into groups based on property parameters, and assigning to each group a set of representative physical-chemical properties. The pseudocomponent approach was used by Yang and Wang (1977), Rasmussen (1985), and Reijhart and Rose

(1982). Yang and Wang assumed that the oil was comprised of eight fractions which were chosen according to carbon number and hydrocarbon type. Rasmussen (1985) used the same criteria in selecting the six oil fractions. Reijhart and Rose selected the 27 pseudocomponents based on the true boiling point curve of the oil. For example, the weight fraction of oil which boils off between 125.7°C and 139.1°C is represented by m-xylene. The properties of the bulk oil depended on the properties of the individual pseudocomponents.

Eastcott et al. (1990) developed a modelling approach called the "matrix method" which was used to characterize the long-term weathering behaviour of oil in a soil environment. The model predicts the time dependent changes in the composition and amount of the oil exposed to evaporation, dissolution and bacterial degradation in soil from a detailed characterization of the parent or original crude oils. Norman Wells crude oil was divided into pseudocomponents according to a volatility-related parameter and chemical class (i.e., normal alkanes, branched alkanes, isoprenoids, aromatics and polars). Physical-chemical properties were assigned to each element based on reported data for chemicals which are known to be present in that group. The pseudocomponents chosen were representative of the compounds found in the oil, and therefore, they approximate the characteristics of the crude oil. Furthermore, the number of components involved is still manageable which makes it feasible to predict the behaviour of oil numerically.

Spill models are excellent for making routine predictions on an oil's changing composition, and physical-chemical properties if they are properly calibrated with laboratory data and validated using data from field situations. Models can be quick

access to information on real spill conditions without having to conduct extensive and expensive field studies.

The ability to model the fate of oil is largely controlled by the availability of equations to characterize the effect of weathering processes on oil composition and properties, and the experimental data of those variables which are largely controlled by analytical capability. Evaporation is a well-characterized process, especially for pure compounds and simple mixtures; however, only approximate equations are available to describe more complex systems such as crude oils. For the dissolution process, descriptive equations also have been developed for pure compounds and multicomponent systems but they are less certain. As for the availability of experimental data, there exist analytical methods which will provide sufficient information on the composition of crude oils and petroleum products.

It is against this background that the present study is undertaken with the specific objective of developing and testing experimental techniques in which crude oils can be subjected to controlled conditions of evaporation and dissolution, and using liquid chromatography to provide detailed characterization of the original and weathered crude oils. The final goal is to establish a modelling approach which predicts the time-dependent changes in the composition and amount of the oils exposed to evaporation and dissolution. Experimental data are obtained and used to calibrate and validate the model.

3.0 MODEL DEVELOPMENT

3.1 Objectives

There are incentives to understand and describe, in quantitative terms, the effect of the evaporation and dissolution processes on the fate of oil spilled in the marine environment. In this study, a simple mathematical model is described which estimates the changes in composition, properties and amount of an oil as it is exposed to spill conditions.

The overall aims of the modelling effort were first to assist in the design of laboratory experiments in which known amounts of oil are subjected to controlled conditions of evaporation and dissolution to obtain changes in oil composition and properties, and second to assess the current analytical techniques which can provide a satisfactory methodology of expressing the initial oil composition in terms of element amounts. Each element is assigned physical and chemical properties, and the fate of each element can be calculated with the use of "mixing rules" such as Raoult's Law. The results obtained from the model must be reconciled with the experimental data. The final task was to investigate different matrix "definitions", that is, different groupings of chemicals with an objective to determining the most appropriate one from analytical and modelling viewpoints, and the optimal number of elements.

Experimental work was undertaken in which evaporation and dissolution were isolated and quantified on an individual basis. To test the effect of evaporation on composition, the gas stripping apparatus was used on oils which have a large proportion of low boiling, volatile hydrocarbons, and the rotating mesh disk apparatus on dense and viscous crude oils. Oil was exposed to dissolution by coating the oil on a solid support

and flowing water over the it for a period of time. The amount of oil which was dissolved in the water was measured. In all cases, the volumes of air or water exposed to the oil were known, and the change in oil composition was assessed by analyzing weathered samples. The data obtained from experiments were used to help test and validate the model for oil spill fate in the marine environment.

3.2 Hydrocarbon Properties and Synthetic Oil Mixture

It is logical to test the model with a system of hydrocarbons which is of known composition and has well-established properties to understand the underlying theory and functioning of the model before applying it to a complex crude oil system containing thousands of chemicals of which many are unknown in structure and properties. This permits observation of the influence of the individual and collective properties of each chemical exposed to controlled evaporation and dissolution conditions on its amount in the oil, and consequently, the effect on the composition and properties of the bulk oil from the change in proportion of chemicals. Moreover, the synthetic oil, a simple hydrocarbon mixture, is helpful in describing the development and use of the model.

The synthetic oil is a mixture of twenty compounds which were chosen according to their chemical class, solubility, relative retention time to those of the normal alkanes, and existence in crude oils. It is comprised of, approximately by mass, 69% saturates, 28% aromatics, and 3% polar (NSO) compounds. Table 3.1 is a compilation of the initial mass percents and property data of the hydrocarbons in the synthetic oil at 25°C. The key parameters, which govern the fate of these hydrocarbons when present in the environment, are tabulated in Table 3.2. They are vapour pressure, water solubility,

Table 3.1 Initial mass percent, carbon number, molecular mass, boiling point, density and molar volume of hydrocarbons in the synthetic oil at 25°C

Compound	Mass percent	Carbon number	Molecular mass (g/mol)	Boiling point (°C)	Density (kg/m³)	Molar volume (cm³/mol)
Normal alkanes						
n-octane	8.0	8	114.2	125.7	7.00×10^2	185.0
n-decane	7.0	10	142.1	174.0	7.30×10^2	229.4
tridecane	4.0	13	184.4	235.4	7.56×10^2	296.0
tetradecane	14.0	14	198.4	252.0	7.63×10^2	318.2
hexadecane	19.9	16	226.4	287.0	7.75×10^2	362.6
octadecane	2.0	18	254.4	317.0	7.77×10^2	407.0
eicosane	2.0	20	282.6	343.0	7.88×10^2	451.4
Branched alkanes						
cyclohexane	4.0	6	84.2	80.7	7.79×10^2	118.2
methylcyclohexane	4.0	7	98.2	100.9	7.70×10^2	140.4
Isoprenoids						
pristane	4.0	19	268.5	296.0	7.85×10^2	429.2
Aromatics						
toluene	6.0	7	92.1	110.0	8.67×10^2	118.2
p-xylene	5.5	8	106.2	138.0	8.60×10^2	140.4
n-propylbenzene	5.1	9	120.2	159.0	8.62×10^2	162.6
1-methylnaphthalene	6.0	11	142.2	245.0	1.03×10^3	169.8
acenaphthene	2.0	12	154.2	278.0		173.1
phenanthrene	2.0	14	178.2	339.0	1.03×10^3	199.2
pyrene	1.5	16	202.3	360.0	1.27×10^3	213.8
NSO compounds						
p-cresol	1.0	7	108.1	202.0	1.03×10^3	125.6
benzo[b]thiophene	1.0	8	134.2	221.0	1.16×10^3	139.7
quinoline	1.0	9	129.2	237.7	1.10×10^3	159.5

Table 3.2 Vapour pressure, aqueous solubility, Henry's law constant and octanol-water partition coefficient of hydrocarbons in the synthetic oil at 25°C

Compound	P^S, Vapour pressure (kPa)	Solubility (g/m³)	C^S, Solubility (mol/m³)	H, Henry's law constant (Pa·m³/mol)	log K_{ow}
Normal alkanes					
n-octane	1.88	6.82×10^{-1}	5.97×10^{-3}	3.15×10^{5}	4.00
n-decane	1.75×10^{-1}	5.20×10^{-2}	4.05×10^{-4}	4.31×10^{5}	5.01
tridecane	4.43×10^{-3}	1.04×10^{-3}	5.64×10^{-6}	7.86×10^{5}	6.65
tetradecane	1.27×10^{-3}	6.55×10^{-4}	3.30×10^{-6}	3.87×10^{5}	7.20
hexadecane	8.98×10^{-5a}	5.21×10^{-5}	2.30×10^{-7}	3.89×10^{5}	8.25
octadecane	7.44×10^{-6}	4.05×10^{-6a}	1.59×10^{-8}	6.22×10^{5}	9.32
eicosane	2.18×10^{-7}	3.11×10^{-7a}	1.10×10^{-9}	1.98×10^{5}	10.39
Branched alkanes					
cyclohexane	1.27×10^{1}	5.75×10^{1}	6.83×10^{-1}	1.86×10^{4}	3.44
methylcyclohexane	6.18	1.60×10^{1}	1.63×10^{-1}	3.79×10^{4}	2.82
Isoprenoids					
pristane					
Aromatics					
toluene	3.80	5.15×10^{2}	6.28	6.05×10^{2}	2.65
p-xylene	1.17	2.21×10^{2}	2.08	5.63×10^{2}	3.18
n-propylbenzene	4.49×10^{-1}	5.22×10^{1}	4.34×10^{-1}	1.03×10^{3}	3.69
1-methylnaphthalene	7.90×10^{-3}	2.84×10^{1}	2.00×10^{-1}	3.96×10^{1}	3.87
acenaphthene	2.87×10^{-4}	3.93	1.40×10^{-1a}	1.06×10^{1}	3.92
phenanthrene	1.61×10^{-5}	1.18	2.52×10^{-2a}	3.59	4.57
pyrene	6.00×10^{-7}	1.35×10^{-1}	1.32×10^{-2a}	9.27×10^{-1}	5.18
NSO compounds					
p-cresol	1.42×10^{-2}	1.80×10^{3}	1.66×10^{1}	8.55×10^{-1}	
benzo[b]thiophene					3.09
quinoline	1.55×10^{-2}	6.11×10^{3}	4.73×10^{1}	3.28×10^{-1}	

a property of the subcooled liquid

Henry's law constant, and octanol-water partition coefficient. The molecular mass, boiling point and density data are obtained from Verschueren (1977) and the CRC Handbook (Weast, 1983-1984). The Le Bas method as described by Reid et al. (1987) is used to estimate the molar volumes. The vapour pressures of the normal and branched alkanes, and most of the PNAs are calculated from the Antoine equation using constants reported by Zwolinski and Wilhoit (1971). The constants for the polar compounds are taken from Lange's Handbook of Chemistry (Dean, 1979). The water solubility values are taken from many reference sources, and for compounds which are solid at room temperature (25°C), the subcooled liquid vapour pressure and water solubility are approximated using the equation given by Prausnitz (1969). The ratio of the solid vapour pressure (or solubility) to that of the liquid is estimated as

$$\ln\left(\frac{P_S^S}{P_L^S}\right) = -\frac{\Delta S}{R}\left(\frac{T_M}{T}-1\right) \qquad [3.1]$$

where P_S^S is the vapour pressure of the solid (Pa), P_L^S is the vapour pressure of the liquid (Pa), ΔS is the entropy of fusion (J/mol·K), R is the gas constant, T_M is the normal melting temperature (K), and T is the system temperature (K). Equation 3.1 can be simplified for a system temperature of 298 K (or 25°C) to the following expression

$$\ln\left(\frac{P_S^S}{P_L^S}\right) = \ln F = -6.74\left(1-\frac{T_M}{T}\right)$$

where the entropy of fusion is shown by Yalkowsky (1979) to be approximately 56 J/mol·K for many organic compounds.

The Henry's law constant, H, is calculated by the following equation

$$H = \frac{P^s}{C^s} \qquad [3.3]$$

The octanol-water partition coefficient, K_{ow}, can be regarded as the ratio of solubility in octanol to solubility in water. The log K_{ow} values are taken from two main references which are Miller et al. (1985) and Coate et al. (1985).

The solubilities of the synthetic oil were measured to be approximately 119 mg/L in freshwater and 77 mg/L in salt water (3.5 wt% NaCl) by purge-and-trap analysis. The high values are attributed to the large proportion of lower aromatic and polar compounds which are toluene, p-xylene, n-propylbenzene, p-cresol, benzo[b]thiophene, and quinoline. These compounds are particularly susceptible to dissolution.

3.3 Matrix Methods

The behaviour of crude oils is difficult to predict with a mathematical model because of their complex nature. It is not feasible to identify every compound; therefore, the crude oil system must be simplified. To decrease the number of compounds which have to be identified and quantified, the oil is divided up into "pseudocomponents". A pseudocomponent is defined as a group of hydrocarbons which is categorized as one compound based upon a set of defined criteria, for example, having similar vapour pressure or water solubility. The "pseudocomponent" concept reduces the number of chemicals involved to a manageable quantity.

The approach described here for modelling oil behaviour is the matrix method which categorizes the compounds in the oil into a two-dimensional matrix according to a volatility-related parameter and their water solubility characteristics. The selection of hydrocarbon grouping is controlled by the analytical techniques available. Gas chromatography is a convenient method for characterizing the volatility of crude oils, and thus, one of the matrix dimensions is the grouping of compounds into rows according to a volatility-related property which is the elution time on a specified non-polar capillary column gas chromatograph. The rows are labelled as elution groups. An elution group is the group of chemicals which elute from the GC column in a specified time interval. In this case, the groups were selected on the basis of the retention times of the normal alkanes whose peaks are easily identified by gas chromatography. They are approximately equidistant and are used to divide up the gas chromatogram. The compounds which elute between two consecutive normal alkanes are considered to be in the same elution group. The elution groups are designated as C_6, C_7, C_8 up to C_{21}. These labels do not necessarily denote the number of carbon atoms in the compounds. For example, the elution group C_7 consists of all compounds which elute after n-hexane (n-C_6) up to and including n-heptane (n-C_7). Benzene which is a C_6 aromatics also belongs in elution group C_7 because it elutes between the C_6 and C_7 normal alkanes. Calibration of the non-polar capillary column GC at defined conditions was made with a normal alkane standard (n-C_5 to n-C_{20}) to determine the lower and upper boundary limits of each elution group.

The concept of elution groups can be more clearly explained with the gas chromatogram of the synthetic oil in Figure 3.1 The chromatogram has been divided up

Synthetic oil

Normal alkane mixture
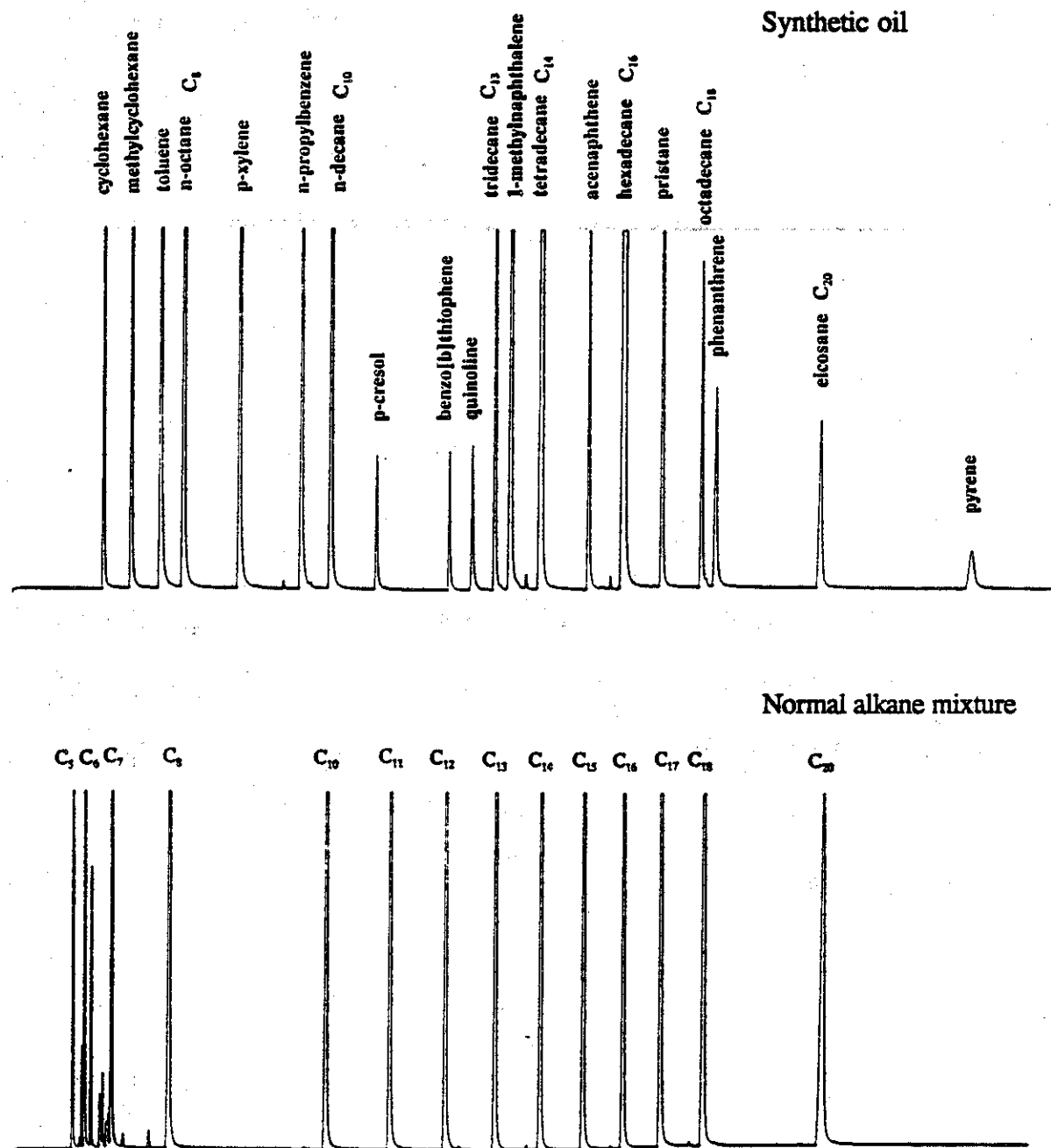
Figure 3.1 Grouping of hydrocarbons in the synthetic oil into elution groups based on the retention times of the normal alkanes.

along the normal alkane peaks which are labelled as C_n where n is the carbon number of the normal alkane. To belong, for instance, to elution group C_8, the compounds must elute after n-heptane (n-C_7) up to and including n-octane (n-C_8). These compounds are methylcyclohexane, toluene and n-octane. Table 3.3 illustrates the placement of the hydrocarbons in the appropriate elution groups which are determined by the elution characteristics of the capillary gas chromatograph used in the study. The table shows the further classification of the hydrocarbons in each elution group according to their chemical class.

As previously mentioned, the second matrix dimension is the grouping of compounds into columns according to their water-solubility characteristics. There are three suggested approaches. A first or "hydrocarbon class" approach is to separate the oil into chemical classes of hydrocarbons which have widely different solubility characteristics. The chemical classes are as follows: normal alkanes, branched alkanes, aromatics and polar compounds. The branched alkane class includes the cycloalkanes and isoprenoids. The isoprenoids can be grouped as a separate chemical class if the biodegradation process is considered in the model because they are more resistant to bacterial degradation than the branched and cyclo-alkanes. The branched and cyclo-alkanes are grouped together because it is difficult to isolate them by gas chromatography, and therefore, the cycloalkanes are assumed to have the properties corresponding to those of the branched alkanes in the same elution group. The aromatics is a well-defined group of hydrocarbons which are more water soluble than other hydrocarbons. The polar compounds which contain nitrogen, sulphur, or oxygen are poorly identified. They are quite water soluble.

Table 3.3 Illustrative matrix showing the placement of hydrocarbons in the synthetic oil in the appropriate elution groups and chemical classes

elution group	normal alkanes	branched alkanes	aromatics	polars
C_6				
C_7		cyclohexane		
C_8	n-octane	methylcyclohexane	toluene	
C_9			p-xylene	
C_{10}	n-decane		n-propylbenzene	
C_{11}				p-cresol
C_{12}				
C_{13}	tridecane			benzo[b]thiophene quinoline
C_{14}	tetradecane		1-methylnaphthalene	
C_{15}				
C_{16}	hexadecane		acenaphthene	
C_{17}				
C_{18}	octadecane	pristane		
C_{19}			phenanthrene	
C_{20}	eicosane			
C_{21}			pyrene	

A second or "solubility" approach is the grouping of compounds in the oil based on mean solubilities or oil-to-water partition coefficients. Both matrix definitions, the "hydrocarbon class" and "solubility" approaches, are investigated with the view of establishing the preferred one.

A third or "HPLC" approach which can be considered is to subject oil to HPLC analysis and separate the compounds into classes based on aromatic ring-number such as saturates, mono-, di-, tri- and polyaromatics, and polar compounds. This method is

similar to the separation of the compounds into class fractions of normal alkanes, branched alkanes, aromatics and polar compounds in the "hydrocarbon class" approach.

The definition of a pseudocomponent differs for each matrix approach. In the "hydrocarbon class" approach, a pseudocomponent is defined as a group of compounds which belong in the same elution group and chemical class. Each pseudocomponent has been assigned properties such as molecular mass, vapour pressure, water solubility, density, molar volume, and water-to-oil and air-to-oil partition coefficients based on reported values for chemicals which are known to be present in that group. Chemicals with known structure and properties serve as representatives for many unidentified compounds grouped in each pseudocomponent. Simple correlations have been developed by Eastcott et al. (1990) for molecular mass, density, vapour pressure and water solubility. They are algebraic functions of the elution group number N and chemical class, and are listed in Table 3.4. The values from the regression equations are presented in matrix form in Appendix A. For compounds which are solid at 25°C, the subcooled liquid vapour pressure and water solubility values were used in deriving the correlations of these properties. The dimensionless air-to-oil and water-to-oil partition coefficients, as discussed later, are the key variables in the model development. They are the ratio of hydrocarbon concentration in air or water to hydrocarbon concentration in oil. The regression equations for these two variables are deduced from those for the above physical properties.

The analytical approach used to divide the oil into pseudocomponents is shown in Figure 3.2. The oil is separated into a pentane-soluble fraction and asphaltenes by precipitation with n-pentane. The asphaltenes are treated as C_{21} aromatics. The soluble

fraction is then subjected to open column chromatographic separation into fractions of saturates, aromatics and polar compounds. Capillary GC analysis of each fraction yields both qualitative and quantitative information on each pseudocomponent in the matrix. The ability to analyze the polar fraction is limited, and many of these compounds are not well-characterized, but the amount found in crude oils is fairly small in comparison with the other two fractions. However, to make the matrix complete, the properties and composition of the polar compounds are estimated from available data.

Table 3.4 Regression equations for physical and chemical properties developed by Eastcott et al.(1990) as a function of elution group number (N) and chemical class.

Molecular Mass (W g/mol)

Saturates	$W = 12.01\ N + 2.016\ (N+1)$
Aromatics	$W = 12.01\ (6 + 4(N\text{-}6)/6) + 1.008\ (6 + 2(N\text{-}6)/6)$
Polars	W for aromatics - 5

Vapour Pressure (P Pa)

Normal alkanes	$P = RT\ 10^{(4.37 - 0.556N)}$
Other saturates	$P = RT\ 10^{(4.24 - 0.509N)}$
Aromatics and polars	$P = RT\ 10^{(3.75 - 0.453N)}$

Water Solubility (C mol/m^3)

Normal alkanes	$C = 10^{(2.368 - 0.566N)}$
Other saturates	$C = 10^{(2.95 - 0.565N)}$
Aromatics	$C = 10^{(2.794 - 0.287N)}$
Polars	C = 4 times C for aromatics

Density of Liquid (D kg/m^3)

Saturates	$D = 634 + 8N$
Aromatics and polars	$D = 581 + 33N$
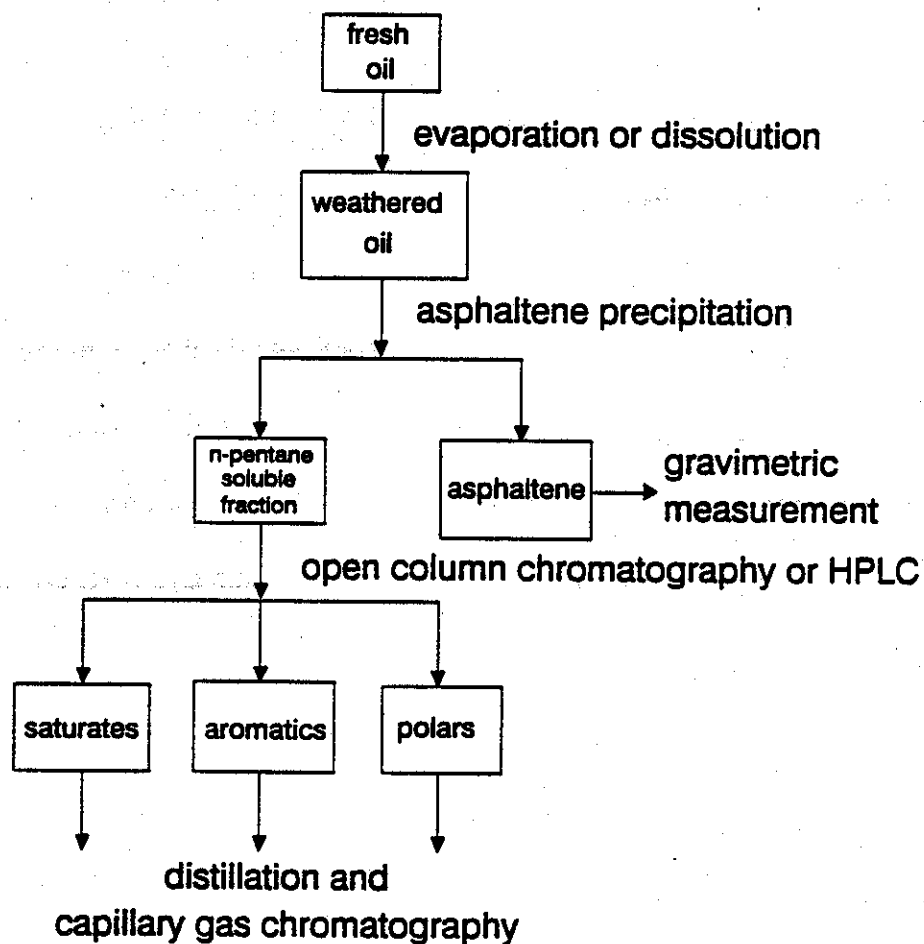
Figure 3.2 Flowchart of analytical method for oil sample separation into chemical classes and elution groups.

An illustration of the "hydrocarbon class" approach is shown in Table 3.5 which gives the matrix of the initial masses of the hydrocarbons for 100 grams of synthetic oil. Exposure to evaporation will cause the depletion of elements in the matrix downward along successive rows from more volatile towards fairly nonvolatile pseudocomponents. Dissolution will result in the loss of the aromatic and polar compounds due to their high water solubility.

The "solubility" approach is the grouping of compounds into rows according to their elution characteristics on a GC, and into columns based on mean solubilities. In this case, a pseudocomponent is defined as a group of compounds which are in the same elution group and solubility class. For each solubility class, a linear correlation equation was developed for each property as a function of elution group number N using data for hydrocarbons compiled by Eastcott et al. (1988). The properties are molecular mass, density, water solubility and vapour pressure. The equations are compiled in Table 3.6 as a function of elution group number N and mean solubility.

Table 3.7 gives an example of the "solubility" approach. It is a matrix of the initial masses of the hydrocarbons in 100 grams of synthetic oil. The columns are divided into classes of mean water solubility with units of grams per cubic metre (g/m^3). For example, the value of 10^2 g/m^3 represents the range in solubility from 50 g/m^3 to 5×10^2 g/m^3. The matrix element at the top left has the highest vapour pressure and water solubility. A near-diagonal matrix resulted with the elements above and below the main diagonal having a mass of zero because, in practice, there do not exist any compounds which have high volatility as well as negligible solubility in water, or negligible vapour pressure and high water solubility. Exposure to evaporation will cause the depletion of

Table 3.5 Matrix for initial mass per 100 g of synthetic oil or percent using the "Hydrocarbon class" approach

elution group	normal alkanes	branched alkanes	aromatics	polars	total
C_6	0.000	0.000	0.000	0.000	0.000
C_7	0.000	4.000	0.000	0.000	4.000
C_8	8.000	4.000	6.000	0.000	18.000
C_9	0.000	0.000	5.500	0.000	5.500
C_{10}	7.000	0.000	5.100	0.000	12.100
C_{11}	0.000	0.000	0.000	1.000	1.000
C_{12}	0.000	0.000	0.000	0.000	0.000
C_{13}	4.000	0.000	0.000	2.000	6.000
C_{14}	14.000	0.000	6.000	0.000	20.000
C_{15}	0.000	0.000	0.000	0.000	0.000
C_{16}	19.900	0.000	2.000	0.000	21.900
C_{17}	0.000	0.000	0.000	0.000	0.000
C_{18}	2.000	4.000	0.000	0.000	6.000
C_{19}	0.000	0.000	2.000	0.000	2.000
C_{20}	2.000	0.000	0.000	0.000	2.000
C_{21}	0.000	0.000	1.500	0.000	1.500
total	56.900	12.000	28.100	3.000	100.000

Table 3.6 Regression equations for physical and chemical properties as a function of elution group number (N) and solubility class.

Solubility class	Water solubiltiy (g/m^3)	Molecular mass (g/mol)	Vapour pressure (Pa)	Density (kg/m^3)
1	10^3			
2	10^2			
3	10			
4	1			
5	10^{-1}	$W = 11.81\,N + 13.78$	$P = RT\,10^{(4.03-0.493N)}$	$D = 608 + 21N$
6	10^{-2}			
7	10^{-3}			
8	10^{-4}			
9	10^{-5}			
10	10^{-6}			
11	10^{-7}			
12	10^{-8}			

Table 3.7 Matrix for initial mass per 100 g of synthetic oil or percent using the "Solubility" approach (ex. 10^2 g/m³ represents the range in solubility from 50 g/m³ to 5×10^2 g/m³)

class and mean solubility (g/m³)	1 10^3	2 10^2	3 10^1	4 1	5 10^{-1}	6 10^{-2}	7 10^{-3}	8 10^{-4}	9 10^{-5}	10 10^{-6}	11 10^{-7}	12 10^{-8}	TOTAL
C_6													0.000
C_7			4.000										4.000
C_8		6.000		12.000									18.000
C_9		5.500											5.500
C_{10}		5.100			7.000								12.100
C_{11}		1.000											1.000
C_{12}													0.000
C_{13}			2.000				4.000						6.000
C_{14}			6.000				14.000						20.000
C_{15}													0.000
C_{16}				2.000					19.900				21.900
C_{17}													0.000
C_{18}									4.000	2.000			6.000
C_{19}					2.000								2.000
C_{20}											2.000		2.000
C_{21}					1.500								1.500
TOTAL	0.000	17.600	12.000	14.000	10.500	0.000	18.000	0.000	23.900	2.000	2.000	0.000	100.000

the pseudocomponents in the same manner described for the first matrix definition. The trend for dissolution of the oil will be the removal of elements along successive columns towards decreasing water solubility.

Comparison of the matrices from the "hydrocarbon class" and "solubility" approaches shows that the total amount of hydrocarbons in each corresponding row is the same because each approach has the grouping of compounds into elution groups as its first matrix dimension. The "solubility" approach is an alternative method of presenting the oil composition information but with a different emphasis from the "hydrocarbon class" approach.

The third or "HPLC" approach has similarities with the "hydrocarbon class" method in that it groups the hydrocarbons in the synthetic oil mixture according to chemical classes and elution groups. Table 3.8 is the assumed matrix for the initial masses of the hydrocarbons in 100 grams of synthetic oil using the "HPLC" approach. The oil is believed to be separated into fractions of saturates, mono-, di-, tri-, and polyaromatics and polar compounds by HPLC. Detailed analyses with chemicals of known hydrocarbon type can help to elucidate the different chemical classes that will result when high performance liquid chromatography is used. It is recommended that the "HPLC" approach be investigated as a method of grouping hydrocarbons for the purpose of modelling oil behaviour. The "HPLC" approach has the advantages of being a fast and routine and could introduce considerable economies of time in the determination.

Table 3.8 Possible matrix for initial mass per 100 g of synthetic oil or percent using the "HPLC" approach

elution group	normal alkanes	branched alkanes	aromatics				polars	total
			mono-	di-	tri-	poly-		
C_6								0.000
C_7		4.000						4.000
C_8	8.000	4.000	6.000					18.000
C_9			5.500					5.500
C_{10}	7.000		5.100					12.100
C_{11}							1.000	1.000
C_{12}								0.000
C_{13}	4.000						2.000	6.000
C_{14}	14.000			6.000				20.000
C_{15}								0.000
C_{16}	19.900			2.000				21.900
C_{17}								0.000
C_{18}	2.000	4.000						6.000
C_{19}					2.000			2.000
C_{20}	2.000							2.000
C_{21}						1.500		1.500
total	56.900	12.000	16.600	8.000	2.000	1.500	3.000	100.000

3.4 Transport Equations

The mass fraction of each element or pseudocomponent can be compiled into a composition matrix which can be converted into a mole or volume basis by the molecular mass and molar volume. The assumption is that each element i contributes to the total vapour pressure P^S and water solubility C^S in proportion to its mole fraction x_i, that is, Raoult's Law applies. The total vapour pressure and water solubility can thus be calculated by adding up the individual values as given by the following equations

$$P^S = \sum x_i P_i^S \qquad [3.4]$$

$$C^S = \sum x_i C_i^S \qquad [3.5]$$

Deviations from ideality can be corrected with an activity coefficient contained in the assumed property of the element.

To calculate the amount remaining of the oil, an assumption has to be made on how the elements influence each other. It is postulated that evaporation and dissolution of an oil occur at a rate controlled by the sum of the individual rates of each element. For an oil exposed to evaporation and dissolution for a period of time dt, the amount of hydrocarbon M_i, moles in each pseudocomponent or element i, changes according to the differential equation

$$dM_i = M_i(-H_{Ei}dQ_E - H_{Di}dQ_D) \qquad [3.6]$$

H_{Ei} and H_{Di} are the dimensionless air-oil partition coefficient and water-oil partition coefficient of the element, that is, the ratio of the concentrations of the element

in air (or water) to oil, and they are the key parameters in the model. They are shown to be

$$H_{Ei} = \frac{P_i^S v_i}{RT} \qquad\qquad [3.7]$$

$$H_{Di} = C_i^S v_i \qquad\qquad [3.8]$$

where P_i^S is vapour pressure (Pa), v_i is molar volume (m³/mol), R is the gas constant

(8.314 Pa·m³/mol·K), T is the system temperature (K), and C_i^S is aqueous solubility

(mol/m³). P_i^S/RT and $1/v_i$ are the concentrations in air and in the oil, respectively.

$C_i^S v_i$ is the ratio of the solubility of element i in water to that in the oil.

Q_E and Q_D are the dimensionless evaporation and dissolution "exposures". They

are controlled by either their respective mass transfer coefficients (k_E and k_D m/h), the

areas (A_E and A_D m), and the oil volume V (m³) or if the air or water becomes

saturated, the flowrates of saturated air and water (G_E and G_D m³/h). These parameters

are defined as follows:

$$Q_E = \frac{k_E A_E t}{V} \quad or \quad \frac{G_E t}{V} \qquad\qquad [3.9]$$

$$Q_D = \frac{k_D A_D t}{V} \quad or \quad \frac{G_D t}{V} \qquad\qquad [3.10]$$

$$dQ_E = \frac{k_E A_E}{V} dt \ \text{ or } \ \frac{G_E}{V} dt \qquad \qquad [3.11]$$

$$dQ_D = \frac{k_D A_D}{V} dt \ \text{ or } \ \frac{G_D}{V} dt \qquad \qquad [3.12]$$

Equation 3.6 can be solved to give each M_i as a function of time. However, a numerical method is required for a rigorous solution because V and v change with time and the concentrations of the nonvolatile compounds increase with the loss of the volatiles. To simplify the solution, it is assumed that A, V and v are constant with time. Therefore, the approximate solution is

$$M_i = M_{io} e^{(-H_{Ei}Q_E - H_{Di}Q_D)} = M_{io} e^{(-Z)} \qquad \qquad [3.13]$$

where

$$Z = H_{Ei}Q_E + H_{Di}Q_D$$

and M_{io} is the initial number of moles and M_i / M_{io} is the fraction remaining. The amount of the oil removed is $(M_{io} - M_i)$ of which attributable to evaporation and dissolution, respectively, are

$$\frac{(M_{io} - M_i)(H_{Ei}Q_E)}{Z} \qquad \qquad [3.14]$$

and

$$\frac{(M_{io} - M_i)(H_{Di}Q_D)}{Z} \qquad \qquad [3.15]$$

If Q_E, Q_D and the initial composition of the oil are known, the amount remaining of each element can be calculated, and the new composition and the total mass lost can be determined. The change in the properties of the bulk oil such as density, viscosity, vapour pressure and aqueous solubility may be estimated from the change in the proportions of the elements present, and the physical-chemical properties assigned to each element. It is important to predict the properties of an oil exposed to the marine environment in order to determine the behaviour of the oil before the appropriate remedial measures can be decided. For example, if the oil's density is found to be greater than the density of seawater, 1024 kg/m³, then the oil is subject to sink into the water column. Before the properties can be calculated, the model must be able give accurate information on oil composition.

Using the "hydrocarbon class" approach, Table 3.9 and 3.10 are illustrative calculations of the change in composition and amount of the original synthetic oil in Table 3.5 for exposure to Q_E of 100000 and Q_D of 4000, respectively. The combined exposure to Q_E of 100000 and Q_D of 4000 will yield the composition matrix shown in Table 3.11.

As mentioned earlier, it is assumed that the crude oil system is an ideal mixture. This simplifying assumption may not hold for such a complex mixture. Two approaches can be considered to account for deviations from ideality. First is to adjust the algebraic correlations for the properties with activity coefficients. The second is to fit each of the exposure parameters Q_E and Q_D in equation 3.13 with a correction factor to obtain the following equation

Table 3.9 Illustrative composition matrix corresponding to an evaporation exposure Q_E of 100000 using the "Hydrocarbon class" approach

elution group	normal alkanes	branched alkanes	aromatics	polars	total
C_6	0.000	0.000	0.000	0.000	0.000
C_7	0.000	0.000	0.000	0.000	0.000
C_8	0.000	0.000	0.000	0.000	0.000
C_9	0.000	0.000	0.022	0.000	0.022
C_{10}	1.934	0.000	0.669	0.000	2.603
C_{11}	0.000	0.000	0.000	0.491	0.491
C_{12}	0.000	0.000	0.000	0.000	0.000
C_{13}	3.864	0.000	0.000	1.820	5.684
C_{14}	13.857	0.000	5.791	0.000	19.648
C_{15}	0.000	0.000	0.000	0.000	0.000
C_{16}	19.882	0.000	1.991	0.000	21.873
C_{17}	0.000	0.000	0.000	0.000	0.000
C_{18}	2.000	3.998	0.000	0.000	5.998
C_{19}	0.000	0.000	2.000	0.000	2.000
C_{20}	2.000	0.000	0.000	0.000	2.000
C_{21}	0.000	0.000	1.500	0.000	1.500
total	43.537	3.998	11.973	2.311	61.819

Table 3.10 Illustrative composition matrix corresponding to a dissolution exposure Q_D of 4000 using the "Hydrocarbon class" approach

elution group	normal alkanes	branched alkanes	aromatics	polars	total
C_6	0.000	0.000	0.000	0.000	0.000
C_7	0.000	3.777	0.000	0.000	3.777
C_8	7.964	3.930	1.461	0.000	13.355
C_9	0.000	0.000	2.562	0.000	2.562
C_{10}	6.997	0.000	3.382	0.000	10.379
C_{11}	0.000	0.000	0.000	0.430	0.430
C_{12}	0.000	0.000	0.000	0.000	0.000
C_{13}	4.000	0.000	0.000	1.572	5.572
C_{14}	14.000	0.000	5.804	0.000	19.804
C_{15}	0.000	0.000	0.000	0.000	0.000
C_{16}	19.900	0.000	1.982	0.000	21.882
C_{17}	0.000	0.000	0.000	0.000	0.000
C_{18}	2.000	4.000	0.000	0.000	6.000
C_{19}	0.000	0.000	1.997	0.000	1.997
C_{20}	2.000	0.000	0.000	0.000	2.000
C_{21}	0.000	0.000	1.499	0.000	1.499
total	56.861	11.707	18.687	2.002	89.257

Table 3.11 Illustrative composition matrix corresponding to a combined exposure of Q_E=100000 and Q_D=4000 using the "Hydrocarbon class" approach

elution group	normal alkanes	branched alkanes	aromatics	polars	total
C_6	0.000	0.000	0.000	0.000	0.000
C_7	0.000	0.000	0.000	0.000	0.000
C_8	0.000	0.000	0.000	0.000	0.000
C_9	0.000	0.000	0.010	0.000	0.010
C_{10}	1.933	0.000	0.444	0.000	2.377
C_{11}	0.000	0.000	0.000	0.211	0.211
C_{12}	0.000	0.000	0.000	0.000	0.000
C_{13}	3.864	0.000	0.000	1.430	5.294
C_{14}	13.857	0.000	5.602	0.000	19.459
C_{15}	0.000	0.000	0.000	0.000	0.000
C_{16}	19.882	0.000	1.972	0.000	21.854
C_{17}	0.000	0.000	0.000	0.000	0.000
C_{18}	2.000	3.998	0.000	0.000	5.998
C_{19}	0.000	0.000	1.997	0.000	1.997
C_{20}	2.000	0.000	0.000	0.000	2.000
C_{21}	0.000	0.000	1.499	0.000	1.499
total	43.536	3.998	11.524	1.641	60.699

$$M_i = M_{i_o} e^{(-H_E f_E Q_E - H_D f_D Q_D)}$$

[3.16]

The correction factors f_E and f_D can be estimated by statistical analysis of the experimental and mathematical model data.

The matrix approaches were implemented in computer programs written in IBM-PC Basic language (Appendix B). The programs require as input data the mass percent of the compounds in the parent or original oil in terms of matrix elements, and the values of the exposure parameters Q_E and Q_D. It then generates a composition matrix of the weathered oil, and a matrix showing the mass lost by each element from the initial 100 gram of oil.

4.0 EXPERIMENTAL

4.1 Materials

The heavy crude oils were supplied by Environment Canada and the US Minerals Management Service. A synthetic oil and an Environmental Protection Service (EPS) standard oil were used to help develop an experimental protocol whereby heavy crude oils may be subjected to controlled evaporation and dissolution conditions.

The physical-chemical properties of the heavy crude oils are listed in Table 4.1. Their densities exceed 900 kg/m^3, but they are less dense than freshwater and salt water which have respective densities of 1000 kg/m^3 and 1024 kg/m^3. Density and viscosity values were taken from Lee et al. (1989). The oils' chemical compositions were characterized by gas chromatography, and their gas chromatograms are shown in Figure 4.1. Table 4.2 gives the composition of the original oils which were obtained by open column chromatographic analysis. California Crude API 15 oil has appreciable amounts of highly volatile and water-soluble hydrocarbons, and a water solubility of approximately 26 mg/L in freshwater and 15 mg/L in salt water. California Crude API 11 oil has slightly less volatile compounds, and half the amount of the very water-soluble hydrocarbons. Bunker C fuel oil consists mostly of the higher molecular weight compounds which account for the low water solubility values in freshwater and salt water. Cold Lake bitumen is a complex mixture of hydrocarbons; the single dominant peak is aromatic in nature.
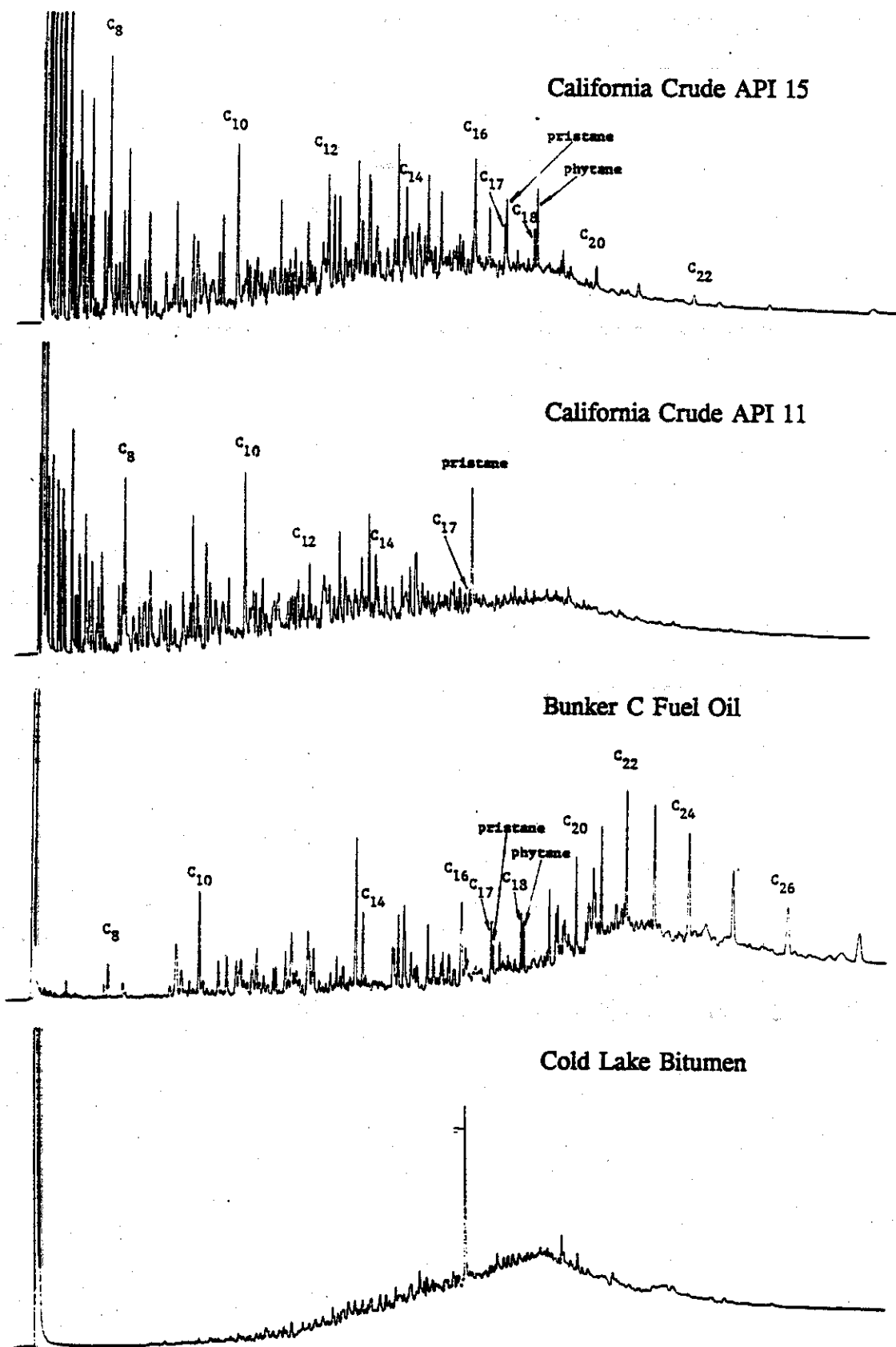
Figure 4.1 Gas chromatograms of heavy crude oils and residual fuels.

Table 4.1 Properties of heavy crude oils and residual fuels

Oil Type	API Gravity	Density @ $22\pm2°C$ (kg/m^3)	Viscosity @ 15°C (cp)	Solubility	
				d.d H_2O (mg/L)	salt H_2O[3] (mg/L)
California Crude API 15 oil	13.2	968	31000	25.7	14.7
California Crude API 11 oil	10.8	978	34000	11.3	9.78
Bunker C fuel oil	12.3	971	48000	4.23	1.95
Cold Lake bitumen	9.8	985	240000	0.26	0.13
EPS[1]	—	836	7.09[2]	34.5	—

[1]Environmental Protection Service (EPS) standard crude oil which was used in preliminary experiments.
[2]measured at 20°C.
[3]3.0 wt% NaCl in salt H_2O.

Table 4.2 Hydrocarbon analysis of heavy crude oils and residual fuels by open column chromatography

Oil Type	Saturates	Aromatics	NSO compounds	Asphaltenes
			(% by weight)	
California Crude API 15 oil	48.3	21.8	5.1	24.8
California Crude API 11 oil	22.5	48.5	5.1	23.9
Bunker C fuel oil	33.2	51.2	5.1	10.5
Cold Lake bitumen	16.6	39.2	24.9	19.3
EPS oil	75.5	18.6	3.6	2.3

4.2 Oil Weathering

4.2.1 Evaporation

Two experimental methods were used for oil evaporation: gas stripping and rotating mesh-disk techniques.

Gas Stripping Technique

The stripping technique was to use a modified version of the gas stripping apparatus (Stiver and Mackay, 1984) which is shown in Figure 4.2. A 250-mL graduated cylinder was fitted with a lid from which a glass tube was extended to the bottom of the container. The lower end of the inlet tube was enclosed except for several pinholes through which air was bubbled. Two gas traps were connected in series to the outlet of the cylinder. These vessels were similarly constructed, but the inlet tubes were open at the bottom. The gas traps were cooled with liquid nitrogen.

Air was provided by the laboratory supply, and was filtered with a molecular sieve trap before it was used. A Scientific Wet Test Meter was used to measure the cumulative air flow through the gas stripping system.

The graduated cylinder was filled with a known mass and volume of oil, and air was bubbled through the oil at a rate of 400 mL/min through the system. The air supply was periodically stopped, and at which time, the remaining mass and volume of the crude oil in the cylinder were measured as a function of the volume of air which flowed passed. In addition, oil samples were analyzed by gas chromatography to quantify the extent to which hydrocarbons were evaporated from oil. The compounds stripped from the oil were recovered by the gas traps and subjected to analyses. The recovery
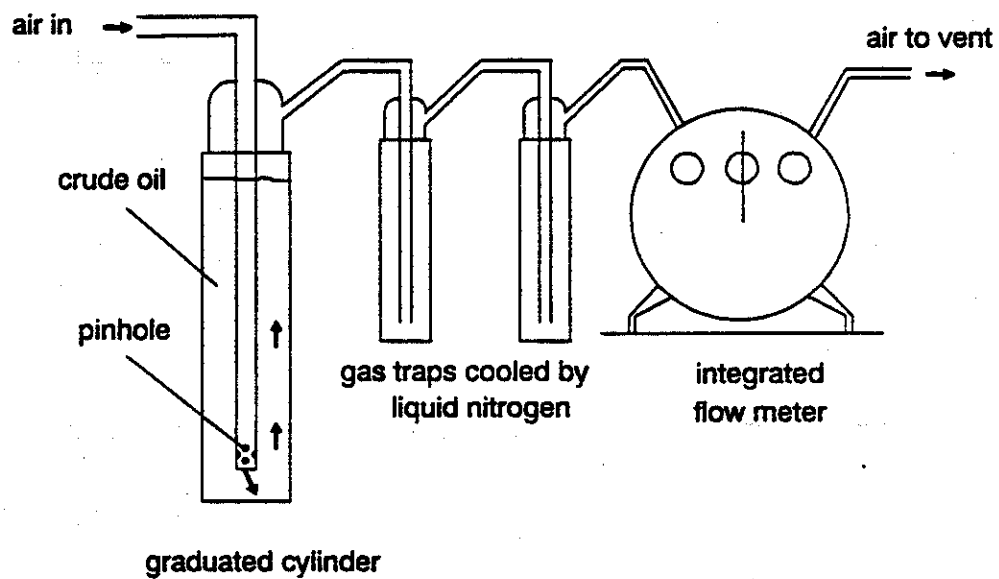
Figure 4.2 Gas stripping apparatus for evaporation.
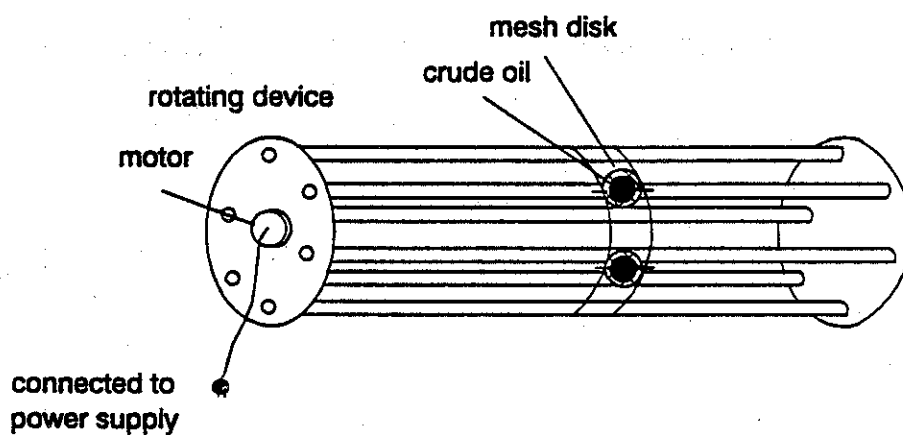
Figure 4.3 Rotating mesh-disk apparatus for evaporation.

efficiency of the evaporated hydrocarbons averaged 90 %. Measurements were thus made of the weathered oils' changing composition, amount, and density as a function of the ratio of exposed air to the initial oil volume which is denoted as Q_E.

Rotating Mesh-disk Technique

A second more rapid method of weathering oil by evaporation was to use a rotating mesh disk apparatus which is illustrated in Figure 4.3. Appropriate amounts of oil (~ 1 gram) were applied to PeCap[®] polyester (Tetko Inc.) mesh disks of 60 mm diameter. These oil-covered disks were secured to the rotating device in which the continuous circular movement of the apparatus prevented the oil from dripping off the mesh disks. The entire system was placed in a dark fumehood, and subjected to turbulent air flow. The effective air flow rate for the system can be determined by comparison of the oil composition data with those obtained from the air stripping experiment. With this method, there is a substantially increased rate of evaporation. Periodically, an oil-covered mesh disk was retrieved for measurements of mass in air and in water, and thus the density of the weathered crude oil can be calculated. Ultrasonic vibration and n-pentane were used to loosen the oil from the mesh disk, and the asphaltenes were precipitated out, filtered and weighed. The pentane-soluble fraction of the oil was subjected to open column chromatography.

To further accelerate the evaporation process, distillation or tray evaporation can be used.

4.2.2 Dissolution

The generator column method was previously reviewed and discussed by Billington et al. (1988) and Shiu et al. (1988) for preparing solutions of single component systems and multicomponent oil systems such as crude oils. Here, this method was used to determine the identity of the dissolved hydrocarbons, and the extent to which they were dissolved as the water to oil volume was increased.

A U-tube generator column was packed with Chromosorb W (mesh size 80/100, Mansville Products Corp.) which was coated with 20 % by volume of oil. Glass wool was plugged into the ends to secure the Chromosorb W in the column. Double-distilled water was pumped with a Beckman solution metering pump through the column at a rate of about 3.0 mL/min. Aqueous samples were collected at intervals and the water-soluble hydrocarbon concentrations analyzed by purge-and-trap GC as a function of the water-to-oil volume ratio Q_D. The cumulative eluted water was measured by weighing. Two experimental runs were undertaken for each oil and were discontinued when the water-to-oil volume ratio reached 4100 and 10000. A schematic diagram of the generator column system is shown in Figure 4.4.

The residual oils from the generator column experiments were extracted from the column with n-pentane and subjected to open column chromatography to determine the identity and amount of hydrocarbons remaining in the oil.

4.2.3 Long-term Weathering of Heavy Oils

To observe the long-term weathering of heavy crude oils on the water surface, a 5-L cylindrical container (300 mm I.D.) was filled with a known volume of distilled
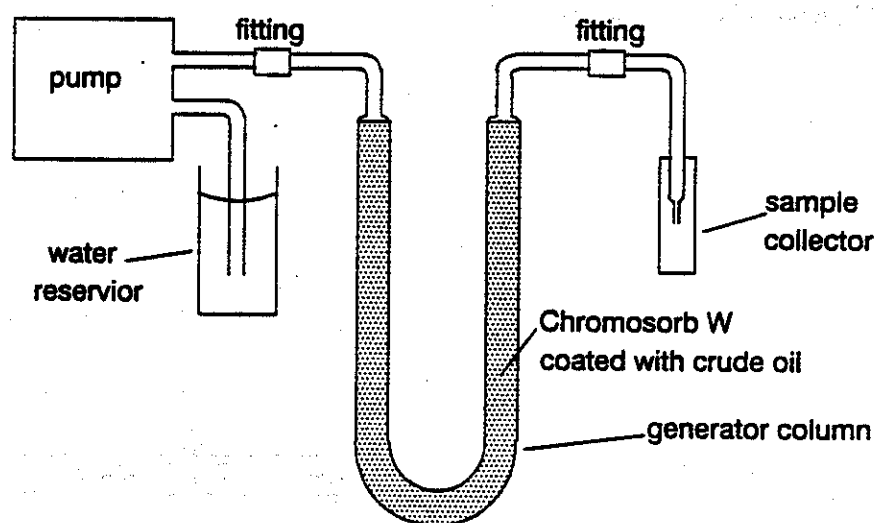
Figure 4.4   Schematic diagram of the generator column method for dissolution.

or salt water (3.0 wt% NaCl) on which approximately 1.5% by volume of oil was poured to form a thin slick (Figure 4.5). The water was continuously agitated with a magnetic stirrer to prevent the oil from adhering to the sides, and some of the water was replaced weekly. The apparatus was set up in the fumehood for a period of two to twelve months. Thus the oil was subjected to evaporation, and dissolution simultaneously. The changing physical characteristics of the oils were observed, and gas chromatographic analyses were performed on oil samples taken from the water surface, and eventually from denser-than-water oil globules in the water column.

4.3 Analysis

4.3.1 Gas Chromatography

Fresh and weathered oils, and their various fractions obtained from open column chromatographic separation were analyzed by gas chromatography. The instrument used was a Hewlett-Packard GC model 5700A equipped with a flame-ionization detector. The column was a 0.75 mm ID x 30 m long glass capillary column coated with SPB-5 supplied by Supelco Canada, Ltd. The operating conditions were as follows: the initial oven temperature was $50^{\circ}C$ for 8 minutes with a temperature programmed rate of $5^{\circ}C/min$, and a final oven temperature of $220^{\circ}C$ for 30 minutes. The injection sample volume was 0.5 μL with a split ratio of 50:1. The peak areas were recorded by a Shimadzu Chromatopac C-R1A integrator using the area normalization method.
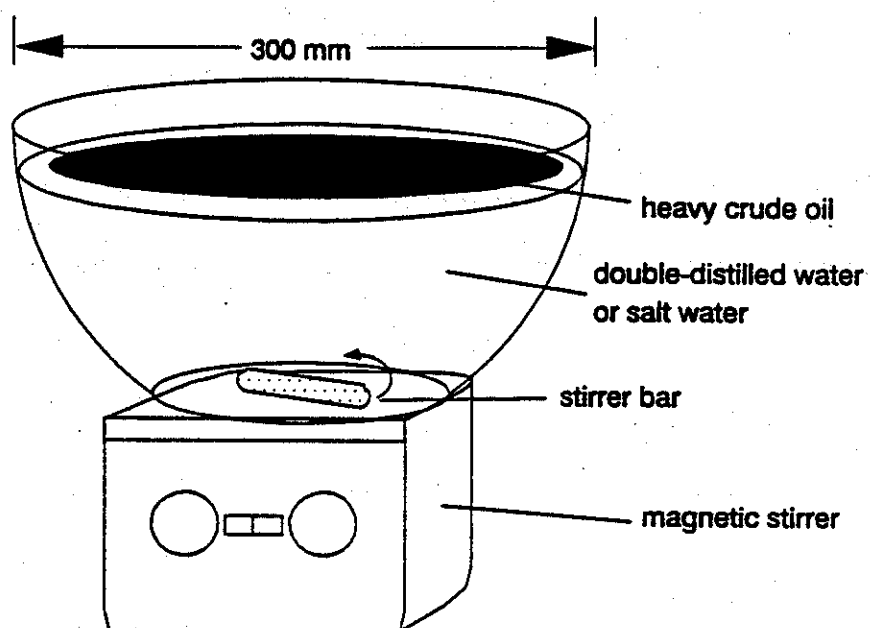
Figure 4.5 Apparatus for the long-term weathering of heavy crude oils.

4.3.2 Open Column Chromatography

The hydrocarbons in crude oils were separated into chemical class by open column chromatography. The fractions obtained by this method are saturates, aromatics, and polar compounds. This analysis facilitates the identification and quantification of the hydrocarbons in the oil.

The pentane-insoluble asphaltenes were precipitated from the oil by the addition of n-pentane (Caledon Laboratories), filtered out and weighed. The de-asphaltened oil was separated into the three fractions using the procedure described by Cook and Westlake (1976). A column was packed with a 1:1 mass ratio of silica to alumina gel. The silica (28-200 mesh) and alumina gel (type F-20, 80-200 mesh) were obtained from Sigma Chemical Co. The order of elution was saturates with n-pentane, aromatics with toluene, and then soluble polar compounds with 1:1 mixture of toluene and methanol. The fractions collected were concentrated by distillation. Subsequent analysis of each fraction by capillary GC yielded information on its composition and amount.

4.3.3 Purge-and-Trap Gas Chromatography

A Hewlett-Packard model 5840A GC with a flame-ionization detector and a HP-7675A purge-and-trap sampler were used to analyze, and thus quantify the hydrocarbon concentrations in aqueous samples. The column was a 0.53 mm ID x 30 m long megabore fused silica capillary column coated with DB-1 (J&W Scientific, Inc.). The oven temperature was set at $50^{\circ}C$ for 10 minutes, and then programmed to increase at a rate of $5^{\circ}C/min$ to a maximum temperature of $200^{\circ}C$ which was maintained for 20 minutes. The detector temperature was at $300^{\circ}C$. The sample volume used was between

2 and 8 mL, and the peak areas were integrated by a HP-5840A GC terminal.

The purge-and-trap technique was used to determine the aqueous solubility of the crude oils. Saturated aqueous oil solutions were prepared by adding oil to water in a separatory funnel with a volume ratio exceeding 1:40. The funnel was shaken gently with a Burrell wrist action shaker for 24 hours and the mixture was allowed to settle for 48 hours before analysis.

4.3.4 Liquid Chromatography

The HPLC system consisted of a Waters Scientific model 510EF solvent delivery system, an U6K injector with a 2-mL sample loop, a 6-part backflush valve, and a model 401 differential refractometer. HPLC-grade n-pentane supplied by Caledon Laboratories was the mobile phase. The column was a semi-preparative 2.5 cm I.D. x 30 cm long stainless steel column packed with dry NH_2 Bondapak. The peak areas were recorded with a HP-3390 integrator. Samples of 100 μL were injected into the system and the fractions eluted with a flowrate of 18.0 mL/min. For elution of polar compounds, the flow through the column was reversed by backflush. The collected fractions were concentrated by micro-distillation.

5.0 RESULTS

5.1 Nature and Accuracy of Analytical Results

Evaporated samples of the synthetic oil were analyzed by gas chromatography in order to obtain information on the changing composition of the mixture. Detector response factors of the hydrocarbons relative to n-hexadecane are given in Table 5.1. Table 5.2 is a compilation of composition data for the synthetic oil up to an evaporative exposure Q_E of 120000. It shows that the masses of higher molecular weight hydrocarbons which are slow to evaporate fluctuate because the detector sensitivity varies for these compounds, caused by bleeding of the gas chromatograph column. For example, pyrene has a mass 1.5 grams in the original synthetic oil It should maintain this mass even as the oil weathers because pyrene has a low vapour pressure of 6.0×10^7 kPa. However, the mass deviates from the value about $\pm 43\%$.

Semi-preparative open column liquid chromatography was the technique used to separate the crude oils into fractions of saturates, aromatics and polar compounds. Gas chromatographic analysis on the resulting fractions yielded quantitative information on the compounds existing in the fractions. Table 5.3 is the composition data of evaporated California Crude API 15 oil by open column chromatography.

Purge-and-trap gas chromatography was used to analyze the changing concentration of the water-soluble hydrocarbons when known volumes of water are passed through the oil. It was used in aqueous solubility determinations of the original and weathered crude oils. The detector limit of the system is approximately 0.01 g/mL.

Table 5.1 Detector response of HP5700A gas chromatograph

Compound	Response factor relative to n-hexadecane	
	Mean	Standard deviation
cyclohexane	0.9388	±0.02363
methylcyclohexane	0.9293	±0.02222
toluene	0.9939	±0.02388
n-octane	0.9063	±0.02001
p-xylene	0.9518	±0.01906
n-propylbenzene	0.9666	±0.01747
n-decane	0.9206	±0.01566
p-cresol	0.7389	±0.01523
benzo[b]thiophene	0.7444	±0.01207
quinoline	0.8556	±0.01145
tridecane	0.9847	±0.01441
1-methylnaphthalene	1.0344	±0.01478
tetradecane	0.9880	±0.01350
acenaphthene	1.0824	±0.05283
hexadecane	1.0000	———
pristane	1.0032	±0.02886
octadecane	0.9727	±0.03891
phenanthrene	0.7887	±0.05497
eicosane	0.7764	±0.03702
pyrene	0.3843	±0.0650

Table 5.2 Experimental composition data for synthetic oil exposed to evaporation up to Q_B =120000

Compound	Mass remaining from initial 100 g of synthetic oil (g)												
	100	99.57	98.22	96.63	94.77	92.32	89.76	87.13	84.41	81.79	79.32	77.12	75.35
cyclohexane	4.000	3.742	3.235	2.846	2.106	1.366	0.868	0.431	0.180	0.063	0	0	0
methylcyclohexane	4.000	3.818	3.562	3.441	2.935	2.341	1.939	1.383	0.915	0.573	0.335	0.164	0.078
toluene	6.000	5.765	5.504	5.444	4.863	4.145	3.702	2.962	2.254	1.675	1.210	0.743	0.472
n-octane	8.000	7.723	7.541	7.659	7.110	6.416	6.118	5.377	4.632	3.978	3.439	2.691	2.094
p-xylene	5.500	5.344	5.266	5.353	5.104	4.800	4.676	4.321	3.965	3.630	3.409	2.964	2.585
n-propylbenzene	5.100	4.987	4.924	5.004	4.896	4.806	4.730	4.577	4.393	4.207	4.170	3.919	3.707
n-decane	7.000	6.865	6.787	6.905	6.822	6.818	6.760	6.657	6.513	6.294	6.466	6.298	6.144
p-cresol	1.000	0.984	0.977	0.968	0.983	1.021	1.005	0.995	0.980	0.946	0.969	0.941	0.943
benzo[b]thiophene	1.000	0.991	0.981	0.961	0.988	1.032	1.003	1.012	0.996	0.985	0.992	0.984	0.972
quinoline	1.000	0.996	1.011	0.973	1.001	1.020	1.006	1.009	0.993	1.005	1.008	1.006	1.002
tridecane	4.000	3.997	3.951	3.881	3.955	4.173	4.084	4.163	4.140	4.063	4.083	4.068	4.053
1-methylnaphthalene	6.000	6.021	5.974	5.809	5.966	6.272	6.102	6.166	6.186	6.072	6.047	6.028	6.012
tetradecane	14.000	14.147	13.918	13.544	13.897	14.593	14.307	14.548	14.419	14.360	14.298	14.250	14.237
acenaphthene	2.000	2.004	2.022	1.947	1.863	1.849	1.873	2.003	1.956	2.021	1.984	1.977	1.967
hexadecane	19.900	20.289	20.106	19.464	19.924	20.288	20.046	20.372	20.099	20.459	20.062	19.984	19.879
pristane	4.000	4.079	4.074	3.939	4.026	4.093	3.999	4.160	4.066	4.080	3.913	3.904	3.885
octadecane	2.000	2.033	2.088	2.031	2.047	2.017	1.933	1.975	2.187	2.007	1.904	1.916	1.940
phenanthrene	2.000	2.092	2.264	2.228	2.149	1.807	1.959	2.245	2.163	1.955	1.817	1.868	1.901
eicosane	2.000	2.039	2.187	2.167	2.164	1.884	1.942	1.739	1.883	2.006	1.920	1.936	1.927
pyrene	1.500	1.653	1.848	2.065	1.921	1.578	1.706	1.036	1.490	1.412	1.295	1.456	1.550
Q_E	0	45	198	402	630	1060	1650	2414	3380	4531	5896	7520	9296

Table 5.2 Experimental composition data for synthetic oil exposed to evaporation up to Q_B=120000 (cont'd)

Compound	Mass remaining from initial 100 g of synthetic oil (g)												
	73.55	71.78	70.23	68.84	67.44	66.14	65.03	64.00	62.73	61.44	60.11	58.76	57.31
cyclohexane	0	0	0	0	0	0	0	0	0	0	0	0	0
methylcyclohexane	0.031	0	0	0	0	0	0	0	0	0	0	0	0
toluene	0.270	0.121	0.051	0	0	0	0	0	0	0	0	0	0
n-octane	1.598	1.048	0.667	0.405	0.212	0.099	0.045	0	0	0	0	0	0
p-xylene	2.267	1.781	1.375	1.055	0.728	0.476	0.311	0.188	0.088	0.039	0	0	0
n-propylbenzene	3.601	3.214	2.851	2.533	2.150	1.815	1.524	1.266	0.892	0.606	0.349	0.178	0.065
n-decane	6.260	5.895	5.523	5.363	4.981	4.693	4.404	4.124	3.553	3.079	2.477	1.909	1.294
p-cresol	0.938	0.905	0.855	0.894	0.860	0.845	0.783	0.767	0.720	0.695	0.641	0.607	0.510
benzo[b]thiophene	0.982	0.945	0.921	0.943	0.911	0.901	0.882	0.875	0.827	0.804	0.751	0.718	0.638
quinoline	1.006	0.996	0.976	0.995	0.979	0.977	0.970	0.974	0.956	0.935	0.919	0.900	0.867
tridecane	4.081	4.025	3.924	4.060	3.984	4.008	3.975	4.008	3.930	3.989	3.925	3.998	3.851
1-methylnaphthalene	6.036	5.894	5.812	5.965	5.850	5.872	5.818	5.837	5.704	5.701	5.570	5.608	5.375
tetradecane	14.196	13.957	13.785	14.239	14.010	14.076	13.962	14.068	13.853	14.071	13.895	14.286	13.915
acenaphthene	1.393	1.901	1.931	1.903	1.883	1.874	1.954	1.942	1.924	1.900	1.871	1.629	1.607
hexadecane	19.620	19.430	19.519	19.403	19.178	19.003	19.681	19.671	19.467	19.392	19.052	19.427	19.318
pristane	3.939	3.927	3.952	3.967	3.963	3.933	3.809	3.691	3.649	3.760	3.694	3.721	3.722
octadecane	1.899	1.953	1.987	1.939	1.961	1.914	1.819	1.757	1.752	1.798	1.759	1.771	1.824
phenanthrene	2.012	2.207	2.149	1.942	2.111	2.087	2.021	1.727	1.912	1.779	1.818	1.591	1.697
eicosane	1.935	1.948	2.079	1.866	1.995	1.897	1.718	1.709	1.777	1.681	1.695	1.559	1.701
pyrene	1.489	1.633	1.872	1.367	1.685	1.669	1.353	1.398	1.727	1.212	1.695	0.857	0.925
Q_E	11532	14368	17310	20541	24258	28771	33951	40128	47346	57222	70365	87508	110160

Table 5.3 Hydrocarbon analysis of California Crude API 15 oil by open column chromatography

Evaporative exposure Q_E	Mass fraction evaporated F_M	Saturates	Aromatics	Polars	Asphaltenes	Total
0	0	48.3	21.8	5.10	24.8	100.00
4170	1.68	19.2	42.4	5.89	31.0	98.32
8330	2.19	19.2	42.3	4.60	31.7	97.81
25000	6.29	14.6	40.1	5.77	33.2	93.71
100000	10.4	18.3	35.5	6.87	28.9	89.60
125000	10.96	16.9	36.5	8.12	27.5	89.04
400000	12.8	15.7	35.7	4.55	31.3	87.20
600000	14.14	12.4	41.6	6.87	25.1	85.86
800000	14.98	17.3	33.7	6.52	33.2	85.02

5.2 Evaporation

The synthetic oil is a mixture of twenty hydrocarbons of which 69% by mass are saturates, 28% aromatics and 3% polar compounds. The synthetic mixture was subjected to evaporation using the gas stripping apparatus up to a Q_E of 120000. Figure 5.1 is a series of gas chromatograms which shows the progressive loss of the volatile compounds. After exposure to Q_E of 120000, cyclohexane, methylcyclohexane, toluene, n-octane, p-xylene, and n-propylbenzene have been substantially depleted from the hydrocarbon mixture because of their high vapour pressures. This resulted in the loss of about 40% by volume of the oil, and an increase of density from 804 kg/m^3 to 846 kg/m^3 as shown in Figure 5.2.

A gas chromatogram of fresh EPS oil is depicted in Figure 5.3. It has an abundance of low boiling, volatile hydrocarbons, and of highly water-soluble compounds
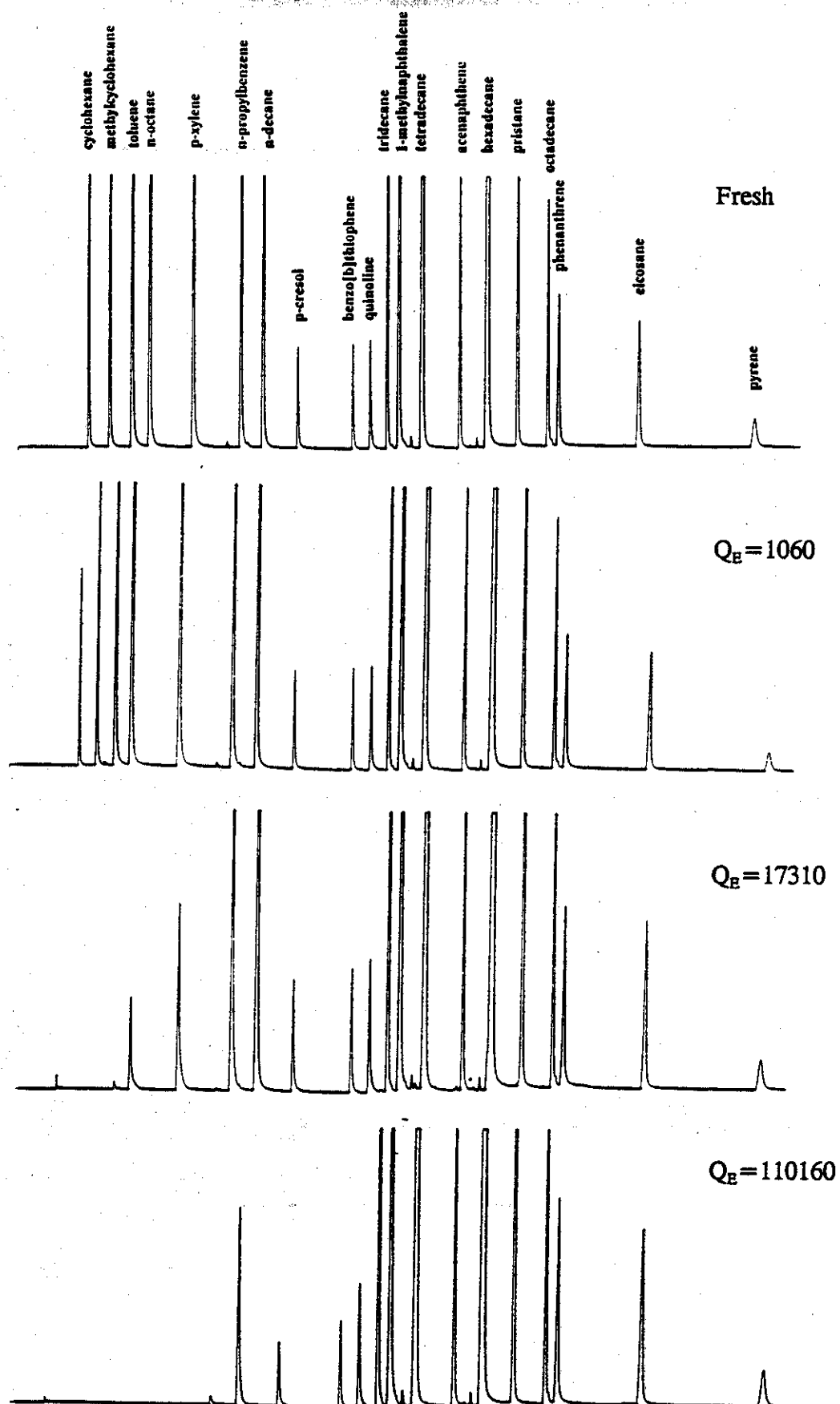
Figure 5.1   Gas chromatograms showing the progressive loss by evaporation of hydrocarbons in the synthetic oil.

Figure 5.2 Density versus air-to-oil volume ratio for the synthetic oil.
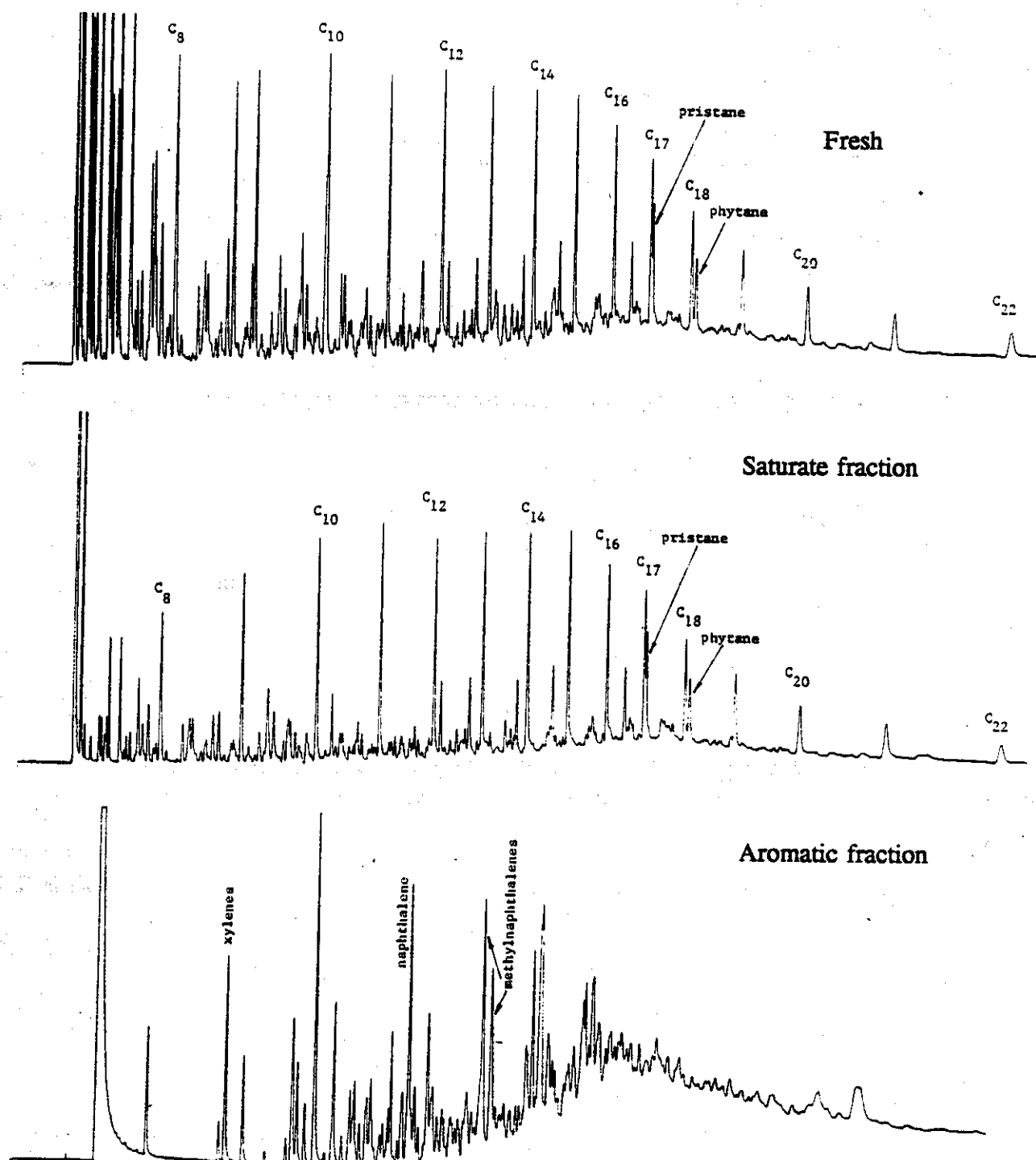
Figure 5.3 Gas chromatograms of fresh EPS oil and its saturate and aromatic fractions.

such as benzene, toluene, ethylbenzene, xylenes, and naphthalene. The saturates and aromatics were separated from the oil by asphaltene precipitation and open column chromatography.

EPS oil was chosen as the crude oil on which preliminary experiments were performed because it is easily handled, and its changing properties and composition can be clearly observed. This oil was subjected to evaporation using the gas stripping apparatus. Figure 5.4 shows the sample chromatograms of the saturate and aromatic fractions for an evaporative exposure Q_E of 8060. The extent of weathering was 24 % by volume of oil evaporated, and its density increased from 836 kg/m^3 to 883 kg/m^3 (Figure 5.5). Comparison between the gas chromatograms of the fresh and weathered saturate fractions revealed the loss of the volatile compounds from C_5 up to C_{10} whereas there was little difference between the fresh and weathered aromatic fractions.

The rotating mesh disk apparatus was found to be most satisfactory for viscous and dense crude oils such as California Crude API 15 oil because they can be coated on mesh disks before exposing them to evaporation. The effective air-to-oil volume ratio of this evaporation system was determined to be 100000 $\pm$ 5000 per day.

Figure 5.6 is a gas chromatogram of a fresh heavy crude oil, California Crude API 15 oil. It has a high asphaltene content of about 25 wt% which accounts for its high viscosity. Its saturate and aromatic fractions reveal that this oil contains large amounts of highly volatile and water-soluble compounds. A series of gas chromatograms shown in Figures 5.7 and 5.8 illustrate in qualitative terms the progressive evaporation of the saturate and aromatic fractions of California Crude API 15 oil with the rotating mesh disk apparatus over a Q_E of 2880000. It can be observed that much of the volatile
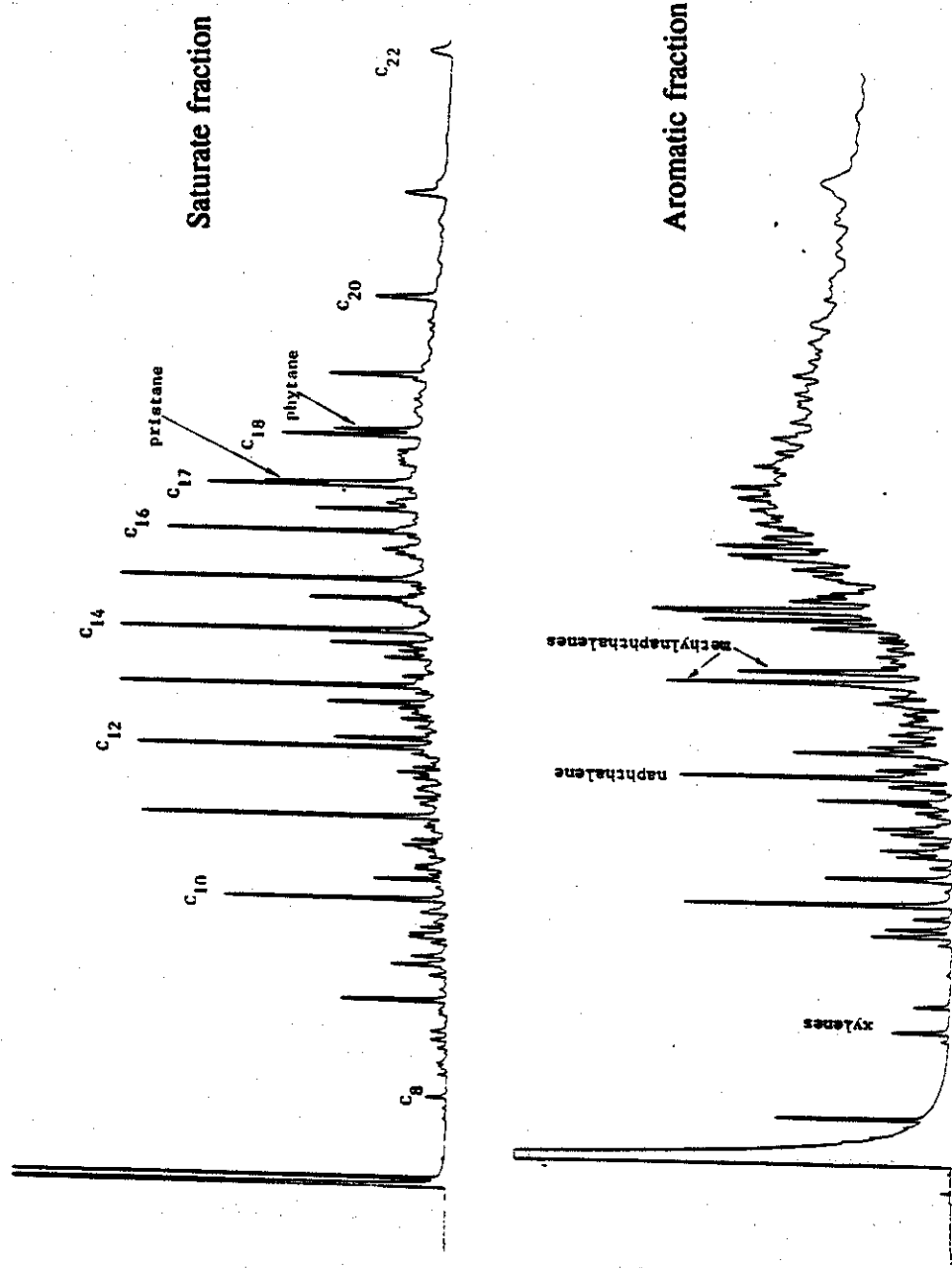
Figure 5.4 Gas chromatograms of the saturate and aromatic fractions of EPS exposed to evaporation of Q_B=8060.
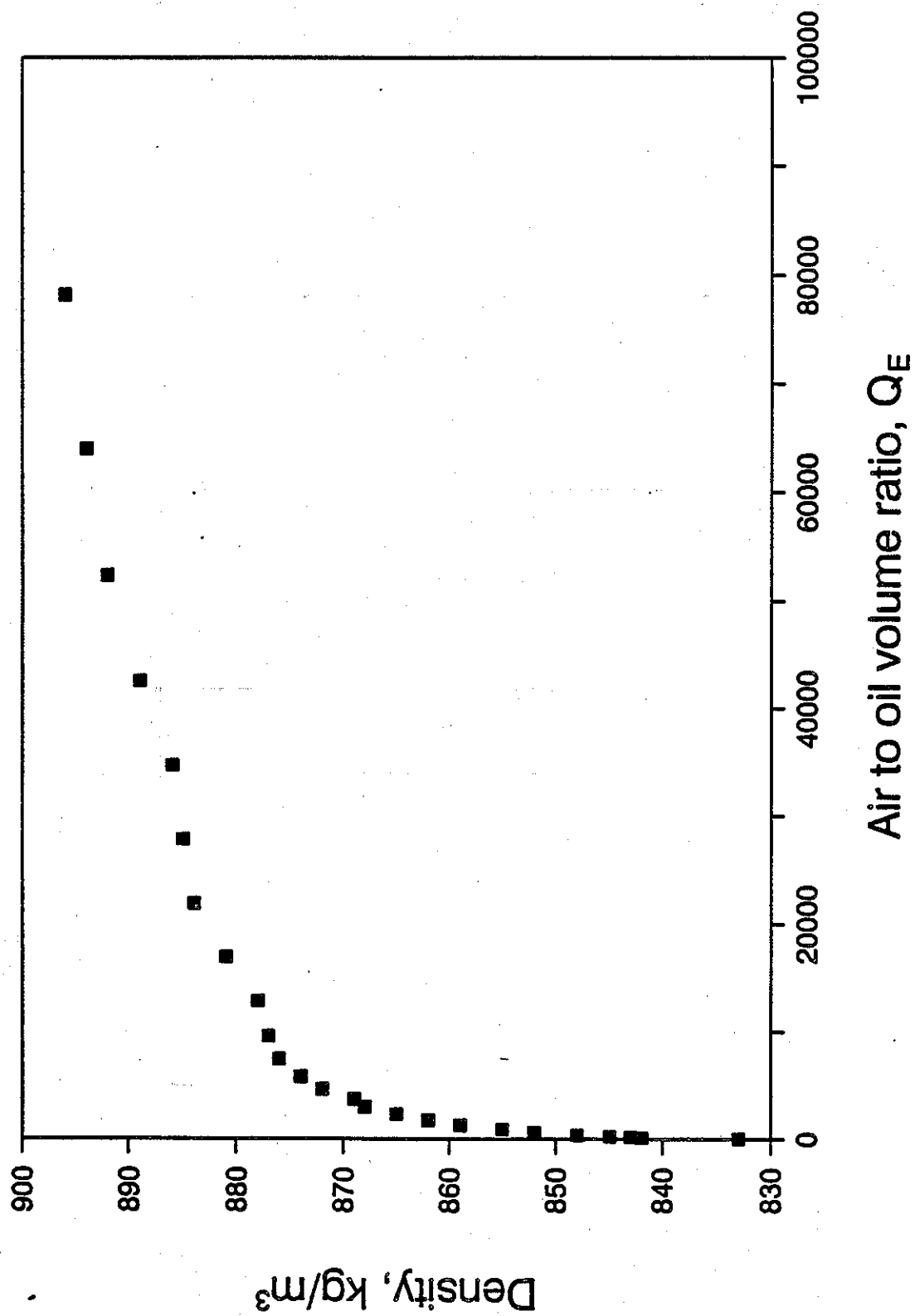
Figure 5.5 Density versus air-to-oil volume ratio for EPS oil.
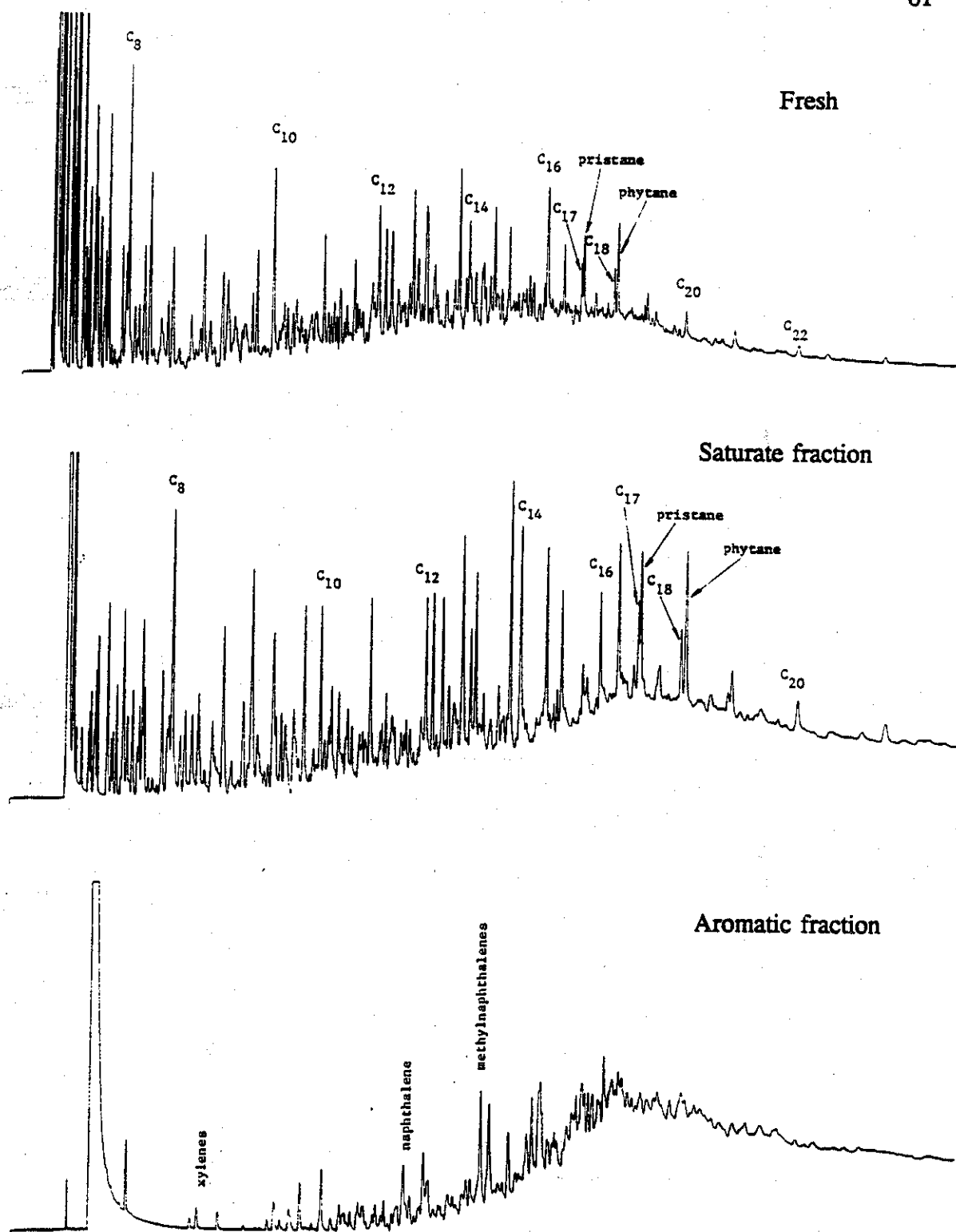
Figure 5.6 Gas chromatograms of fresh California Crude API 15 oil and its saturate and aromatic fractions.
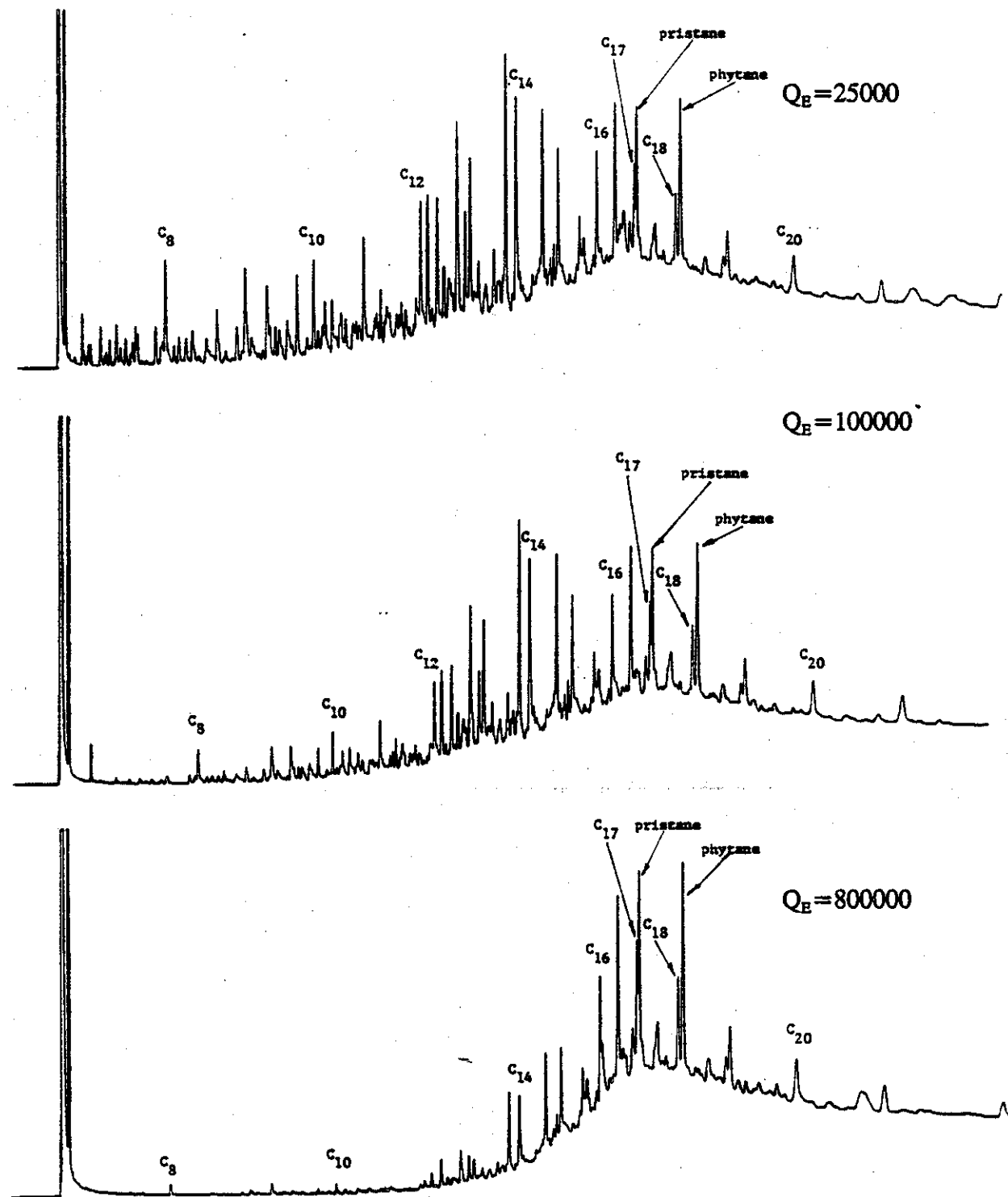
Figure 5.7 Gas chromatograms showing the progressive evaporation of the saturate fraction of California Crude API 15 oil.
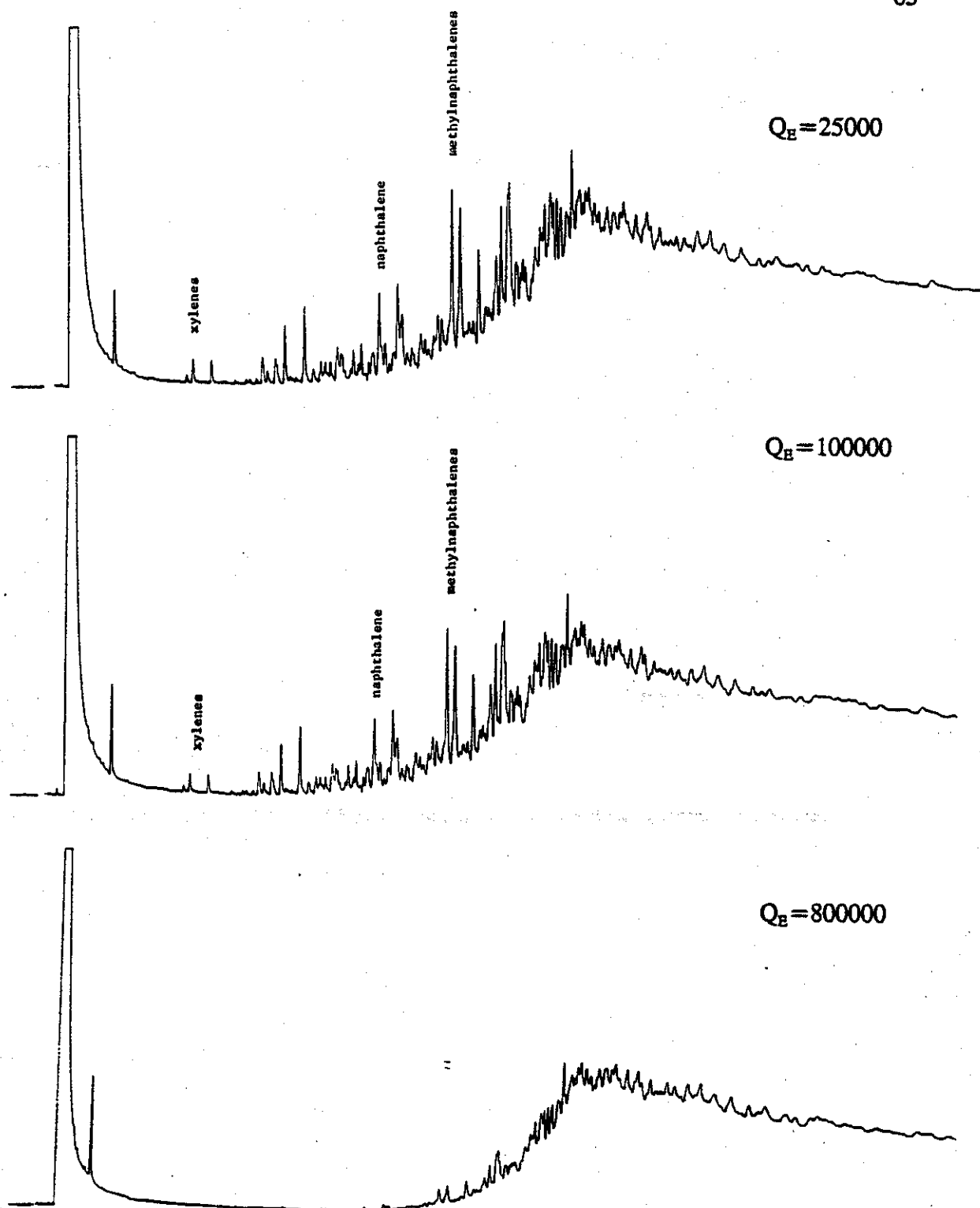
Figure 5.8 Gas chromatograms showing the progressive evaporation of the aromatic fraction of California Crude API 15 oil.

hydrocarbons from C_5 to C_{14} have been lost. The density increased from 968 kg/m^3 to 1015 kg/m^3 (Figure 5.9).

The gas chromatograms of the original California Crude API 11 oil, Bunker C Fuel oil and Cold Lake Bitumen and their saturate and aromatic fractions are not discussed in detail here, but for completeness are given in Appendix C.

5.3 Dissolution

For exposure to dissolution, the synthetic oil was contacted with water in a generator column. Figure 5.10 gives the gas chromatograms of the synthetic oil exposed to a dissolution exposure Q_D of 4100 and 10000. The chromatograms show the depletion of the polar compounds, p-cresol, benzo[b]thiophene and quinoline which have solubilities greater than 1000 g/m^3. The next most water-soluble hydrocarbons are the aromatics: toluene, p-xylene and n-propylbenzene which are shown to be removed by dissolution at a Q_D of 10000. Figure 5.11 illustrates the trend of the synthetic oil's solubility versus water-to-oil volume ratio Q_D. The solubility of the synthetic oil decreased from 119 mg/L to about 2.4 mg/L as a result of the loss of the very soluble polar and aromatic compounds.

Fresh EPS oil also was contacted with water in a generator column. The gas chromatograms of the saturates and aromatics for Q_D of 10000 are shown in Figure 5.12. Comparison between the fresh and weathered aromatic fractions shows that the water-soluble aromatics were depleted, but there was little composition change in the saturate fraction. Analysis by the purge-and-trap technique revealed that the aqueous solubility of the oil decreased from 34.5 mg/L to 1.0 mg/L. The water-soluble fractions
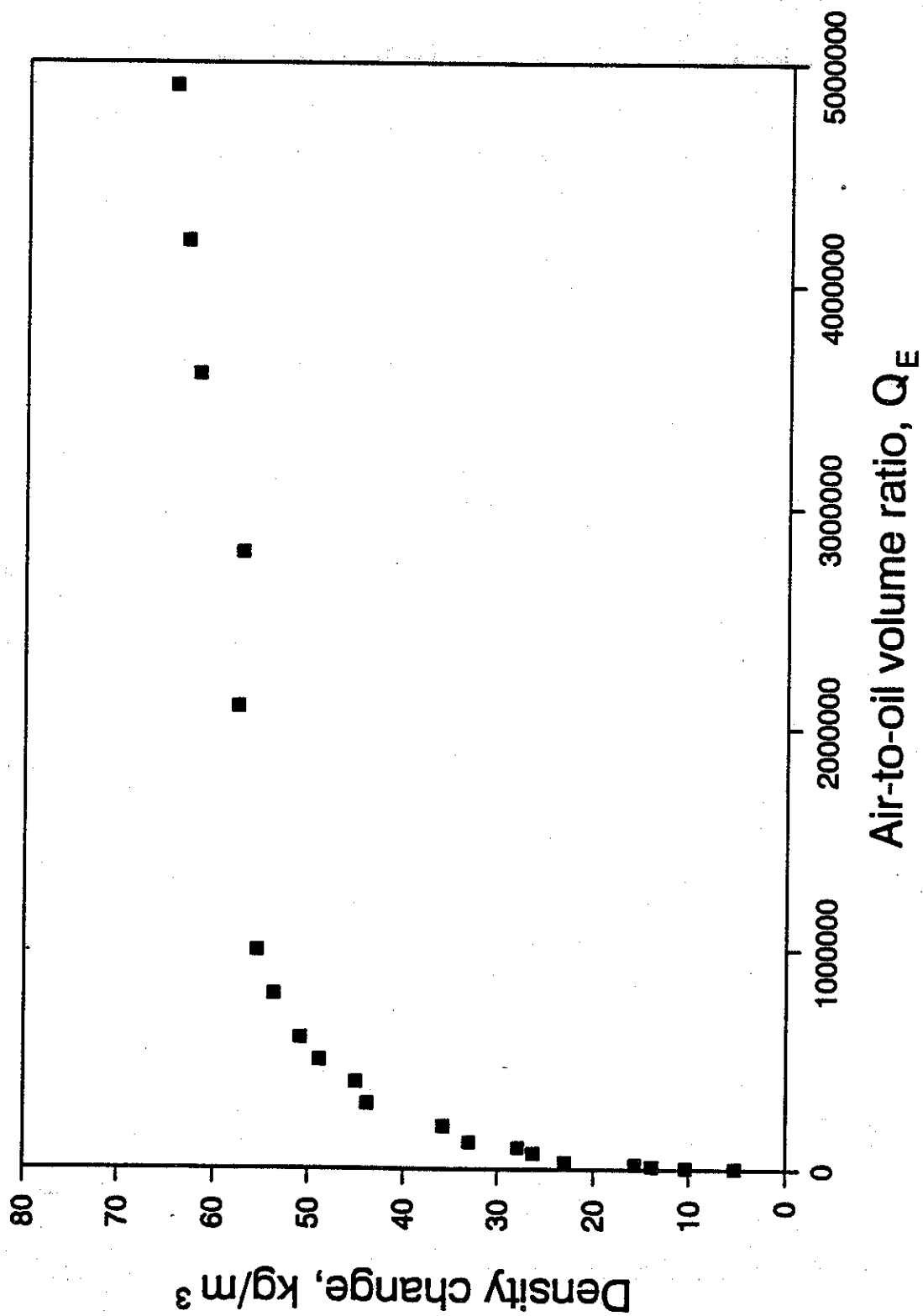
Figure 5.9 Density change versus air-to-oil volume ratio for California Crude API 15 oil.
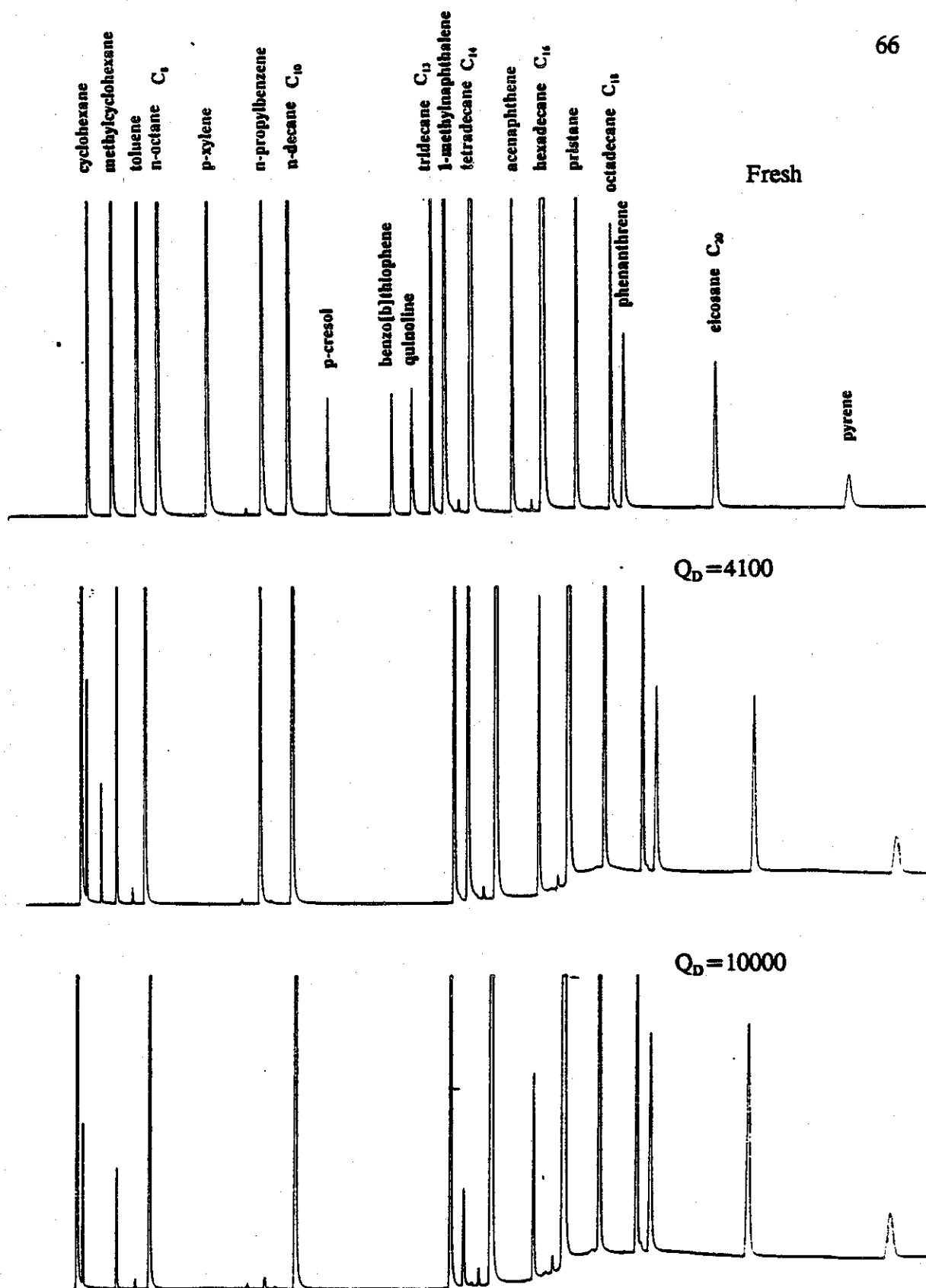
Figure 5.10 Gas chromatograms of the synthetic oil exposed to dissolution up to a Q_D of 10000.
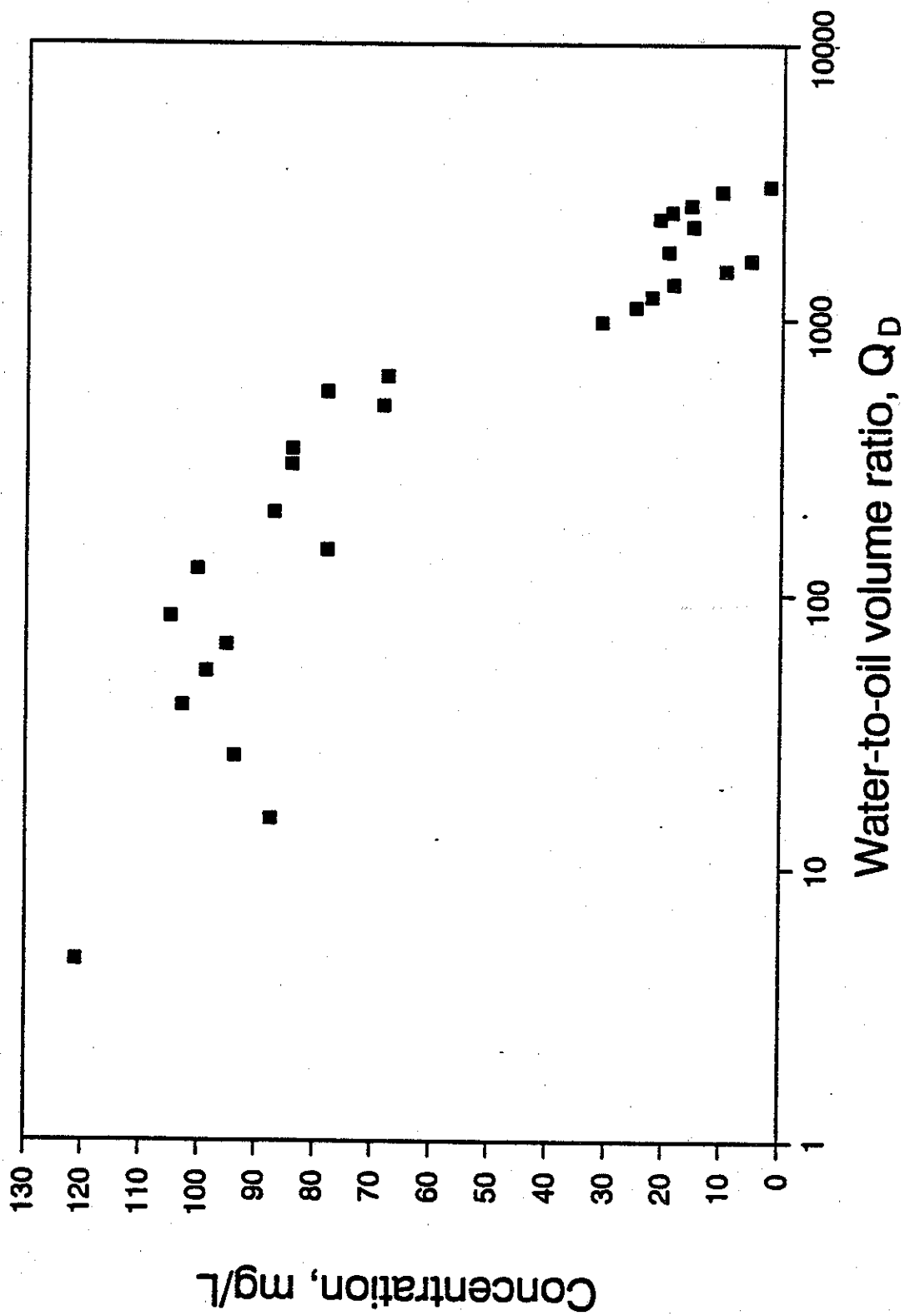
Figure 5.11 Solubility versus water-to-oil volume ratio for the synthetic oil.
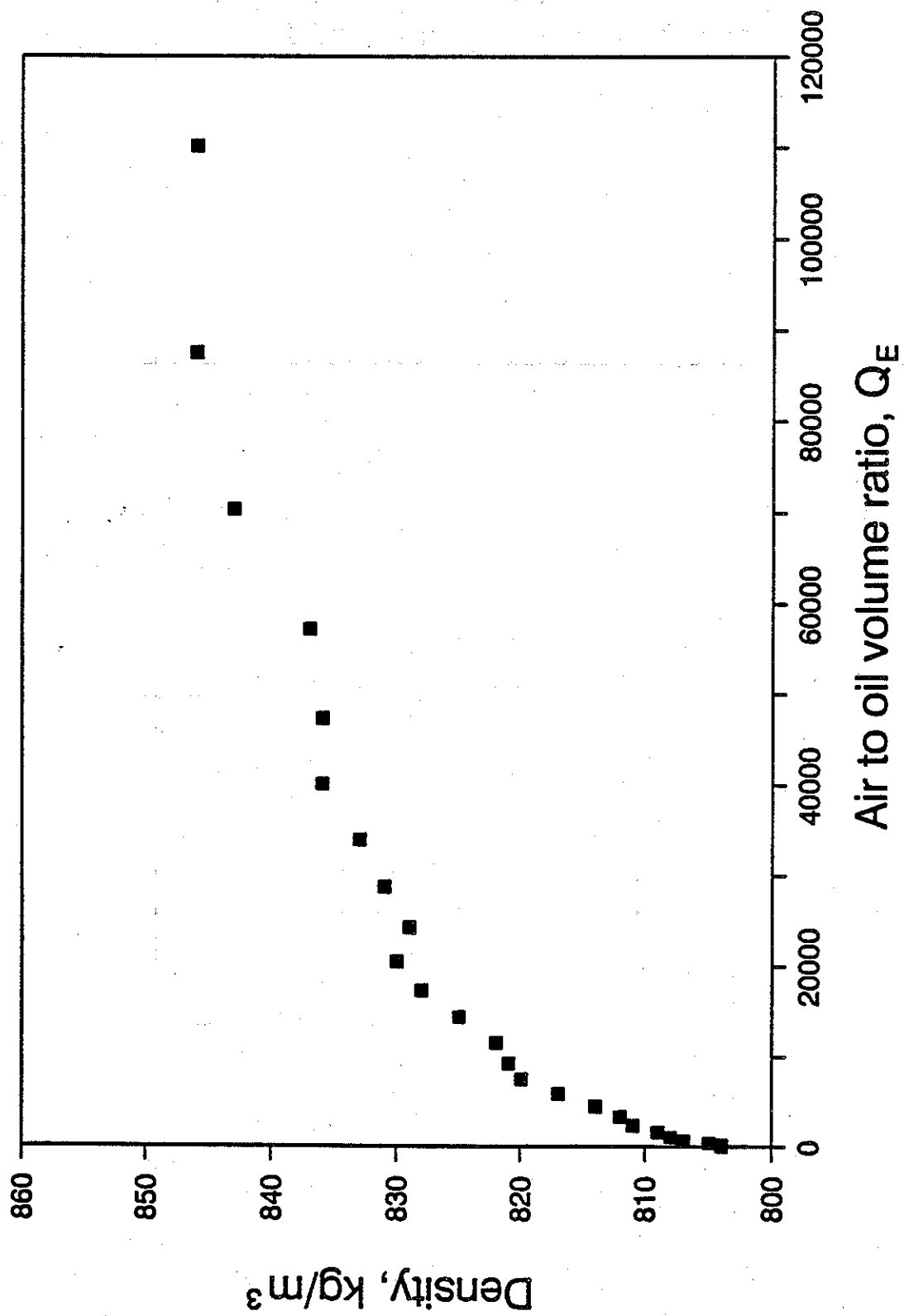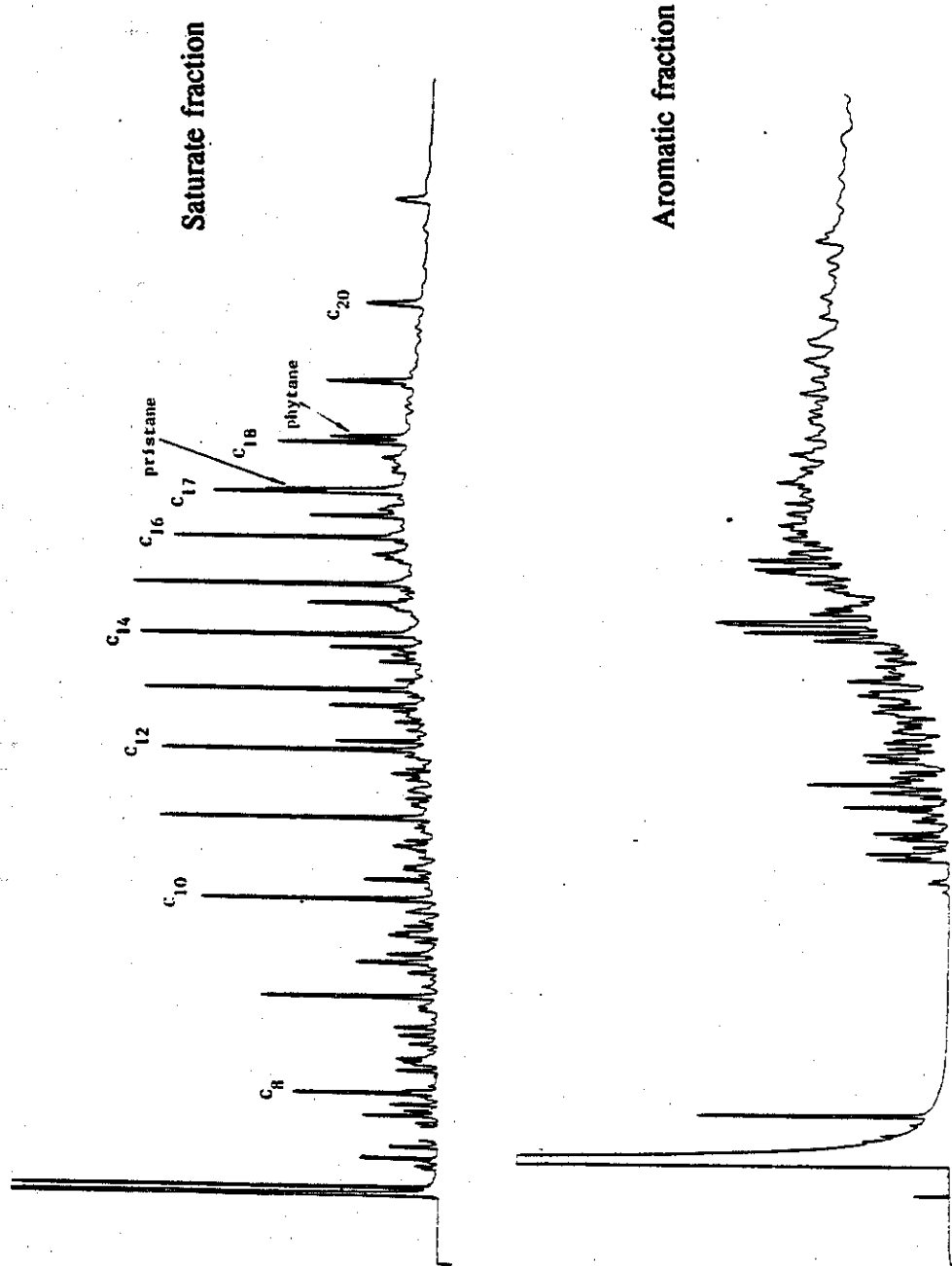
Figure 5.12 Gas chromatograms of the saturate and aromatic fractions of EPS oil exposed to dissolution of $Q_b = 4100$ and 10000.

(WSFs) of the fresh and weathered oil are given in Figure 5.13 which shows that most of the volatile, water-soluble hydrocarbons such as benzene, toluene, ethylbenzene, and o-, p- and m-xylenes were depleted by dissolution. Figure 5.14 gives the trend of the solubility of EPS oil versus the water to oil volume ratio Q_D. The solubility decreased with the depletion of the water-soluble aromatics.

5.4 Long-term Weathering of Heavy Crude Oils

California Crude API 15 oil was subjected to evaporation and dissolution on a water surface in long term weathering experiments. Spreading of the California Crude API 15 oil slick in distilled water occurred within several hours. In salt water, it spread to a lesser extent. The formation of a visible skin or crust was observed after two weeks. Tiny air bubbles gradually appeared on the oil surface in both situations. After three months a 30-mm diameter oil droplet formed below the water surface and detached from the original mass in the distilled water experiment. This oil globule proved to be denser than the water because it sank into the water column. Further submergence of oil mass was observed in the next two months.

In the fifth month, an oil sample from the water surface was taken for gas chromatographic analysis. In addition, the first oil droplet was retrieved and frozen in the effort to obtain samples of the its skin/crust and interior for analysis. It proved difficult to obtain a crust sample because it was very thin, certainly less than 1 mm thick. Figure 5.15 illustrates the five-month weathering of the oil on the water surface and in the water column. The sunken oil was less weathered than the exposed oil on the water surface; the latter was depleted of all hydrocarbons up to C_{16}. Therefore, once

Fresh

n-pentane

n-heptane

benzene

toluene

ethylbenzene

p-,m-xylenes

o-xylene

substituted benzenes

naphthalene

Weathered

substituted benzenes

naphthalene
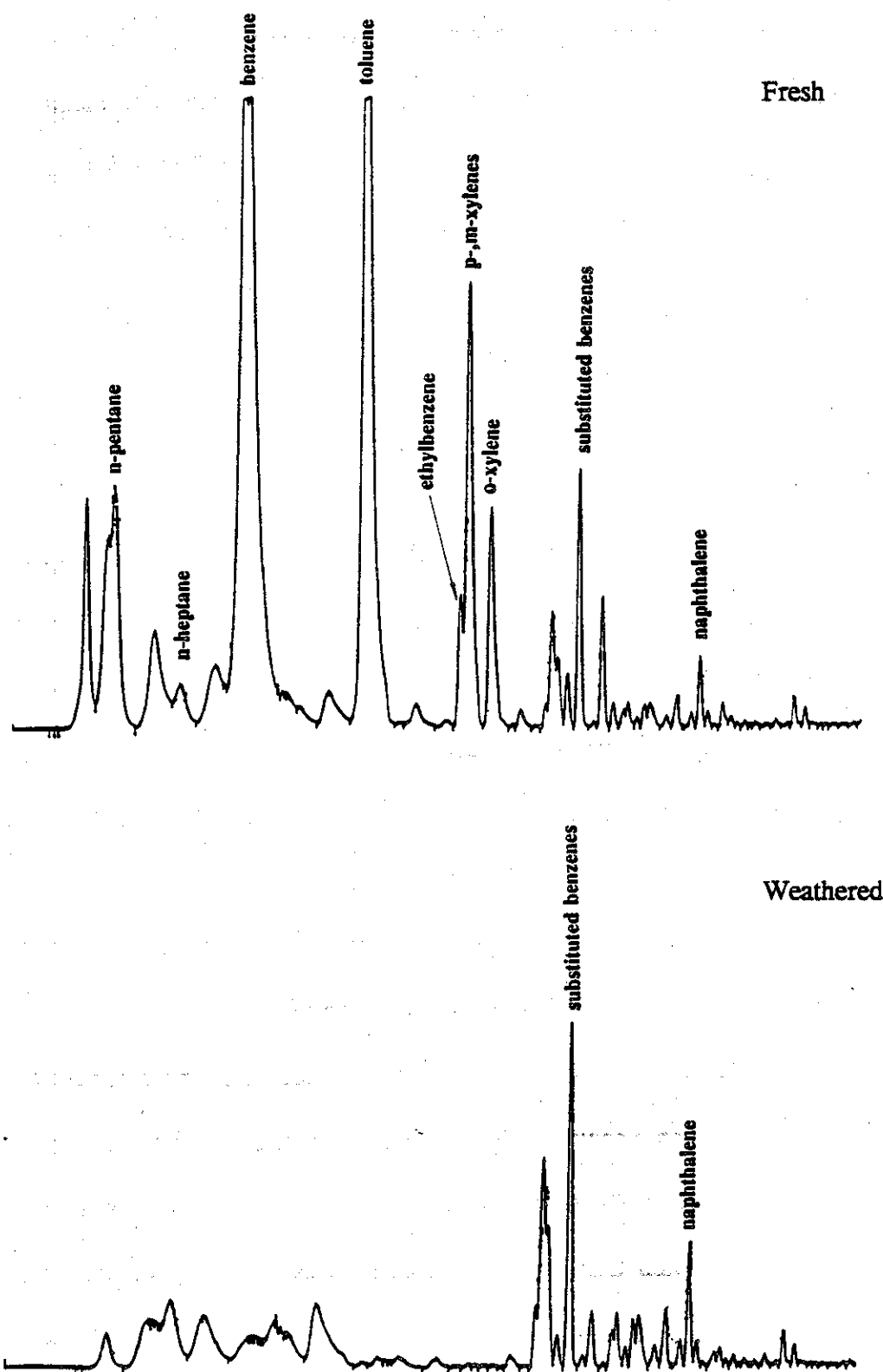
Figure 5.13 Water-soluble fractions of fresh and weathered EPS oil exposed to dissolution.
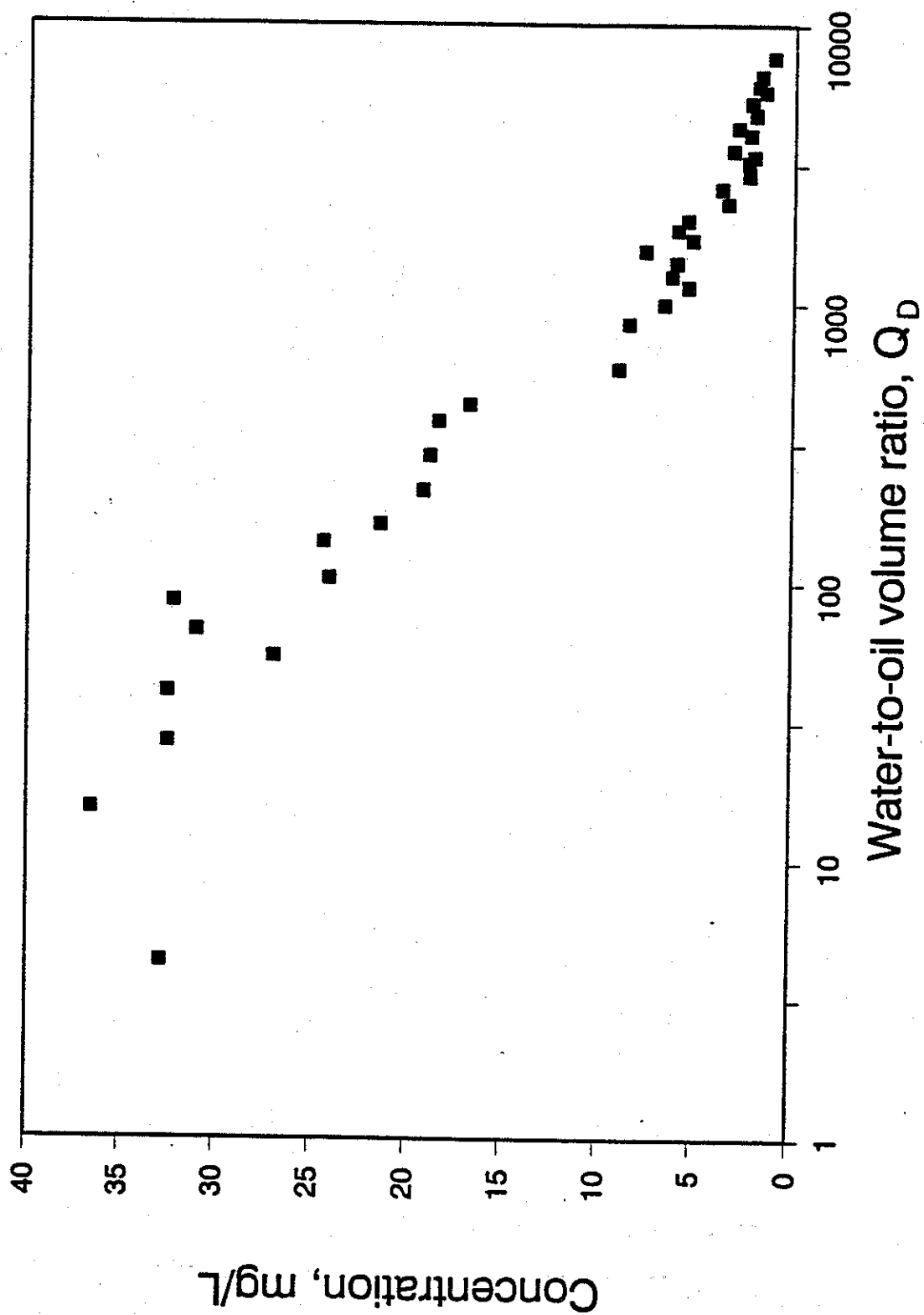
Figure 5.14 Solubility versus water-to-oil volume ratio for EPS oil.
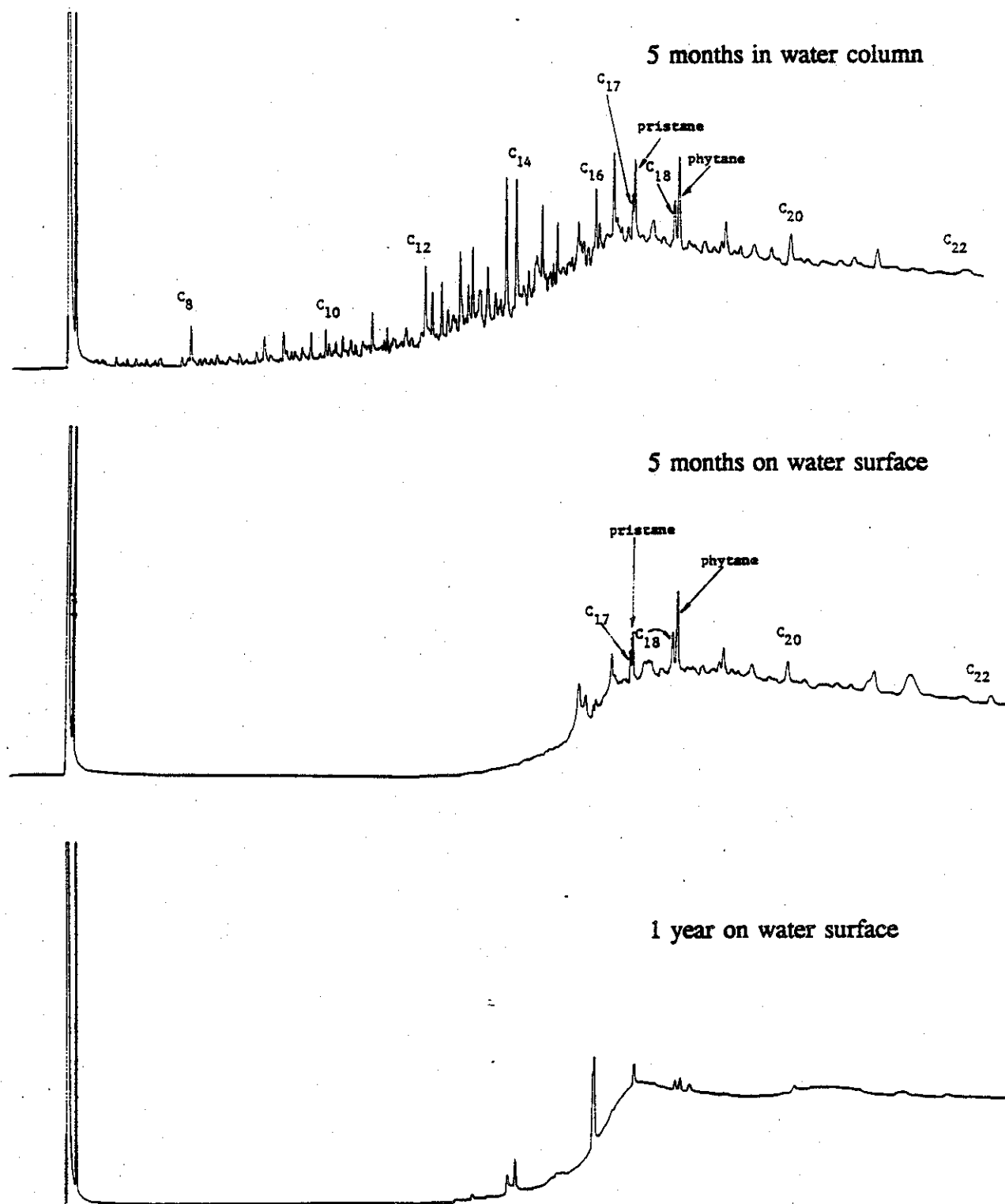
Figure 5.15 The long-term weathering of California Crude API 15 oil.

submerged the oil was subjected to only dissolution which only causes a slight change in composition.

An oil sample taken in the twelfth month showed a very thin layer of oil which was light brown on the underside. This may be a result of degradation by bacteria present in the water column. Gas chromatographic analysis shows that the oil layer consisted of only very high molecular weight compounds such as asphaltenes. Microbial degradation which is an important process in the latter stages of weathering may have occurred since no effort had been made to maintain sterile conditions. The water column became cloudy after five months.

In the course of the experiments, there was no formation of water-in-oil emulsions or "tar balls".

6.0 DISCUSSION

6.1 Contributions and Constraints of Analytical Methods

The ability to understand and model the fate of oils is constrained by the performance of available analytical methods. It is therefore appropriate to discuss first these methods, especially their limitations. The synthetic oil which is the easiest to analyze was a mixture of twenty hydrocarbons which contained 69% saturates, 28% aromatics, and 3% polar compounds by mass. It had no asphaltenic content. The composition of this oil can be analyzed with a nonpolar capillary column gas chromatograph without prior preparative separation of the mixture. The GC detector response factors of the hydrocarbons relative to hexadecane are given in Table 5.1. It was assumed that hexadecane did not evaporate in order to calculate the percentage of an individual hydrocarbon remaining after exposure to weathering processes. Reliable data can be obtained for a simple synthetic oil of this type which consists of known hydrocarbons having well-established physical and chemical properties.

A crude oil consists of thousands of compounds, most of which have not been identified, and therefore, their properties are unknown. There are currently no analytical methods which give a complete description of the composition of crude oils. It is necessary to group the compounds in the oil into pseudocomponents which are defined by a set of criteria. The selection of the pseudocomponents is controlled by the available analytical methods. The analytical approach was to subject the oil to a semi-preparative separation, for example, column chromatographic or HPLC class group-type separation, prior to instrumental analyses by gas chromatography.

EPS standard oil was subjected to open column liquid chromatography to separate

the oil into fractions of saturate, aromatic, and polar compounds. The bulk oil, and the saturate and aromatic fractions were analyzed by GC. The compounds in each fraction were grouped into pseudocomponents according to their retention times relative to those of the normal alkanes. Since the identities of many of the hydrocarbons are unknown, it is not possible to determine the GC detector response factors for all the compounds. It was, therefore, assumed that the response factor for all compounds in the crude oils is unity for calculating the amount remaining of each pseudocomponent. This may introduce an error in the mass by a factor of 2.5 for high molecular weight hydrocarbons such as pyrene.

Tables 6.1 and 6.2 give the matrices for the initial composition on a mass basis of EPS standard oil, and for the experimental composition after an evaporative exposure of 8060, respectively using the "hydrocarbon class" approach. There is clearly depletion of the volatile normal and branched alkanes, and aromatics by evaporation. However, the composition data for California Crude API 15 oil which tabulated in Table 5.3 shows some inconsistencies. The asphaltenic mass of the oil should remain constant as the oil is weathered by evaporation because asphaltenes are very nonvolatile. However, the asphaltenic content for the same crude oil varied between samples. The aromatic fraction showed increases in mass as the oil was weathered. The error is believed to be experimental in nature, and it is suspected that it occurred during the open column chromatographic separation and micro-distillation steps in which the volatile saturates were lost by evaporation. The gas chromatograms of the bulk oil, and the saturate and aromatic fractions are shown in Figure 5.3. Comparison between the bulk oil and the fractions shows that some of the volatile compounds in the saturate fraction have been

Table 6.1 Matrix for initial mass per 100 g of EPS oil or percent using the "Hydrocarbon class" approach

elution group	normal alkanes	branched alkanes	aromatics	polars	total
C_6	0.437	0.000	0.000	0.000	0.437
C_7	1.176	1.671	0.000	0.000	2.847
C_8	1.856	2.915	0.000	0.000	4.771
C_9	2.011	4.110	0.427	0.000	6.548
C_{10}	2.692	5.354	0.832	0.000	8.878
C_{11}	2.614	3.887	1.488	0.000	7.989
C_{12}	2.400	2.721	1.324	0.360	6.805
C_{13}	2.332	3.925	0.809	0.360	7.426
C_{14}	2.545	2.963	1.553	0.360	7.421
C_{15}	3.003	4.498	2.287	0.360	10.148
C_{16}	2.118	2.429	2.407	0.360	7.314
C_{17}	1.798	4.877	2.341	0.360	9.376
C_{18}	1.516	4.013	2.680	0.360	8.569
C_{19}	1.244	1.729	1.783	0.360	5.116
C_{20}	1.002	0.000	0.669	0.360	2.031
C_{21}	0.846	0.818	2.300	0.360	4.324
total	29.590	45.910	20.900	3.600	100.000

Table 6.2 Matrix for the experimental composition of EPS oil exposed to Q_E of 8060 using the "Hydrocarbon class" approach

elution group	normal alkanes	branched alkanes	aromatics	polars	total
C_6	0.000	0.000	0.000	0.000	0.000
C_7	0.000	0.000	0.000	0.000	0.000
C_8	0.090	0.000	0.000	0.000	0.090
C_9	0.842	0.373	0.000	0.000	1.215
C_{10}	1.783	2.929	0.123	0.000	4.835
C_{11}	2.264	3.297	0.665	0.000	6.226
C_{12}	2.348	2.633	0.833	0.350	6.164
C_{13}	2.415	4.190	0.466	0.350	7.421
C_{14}	2.597	3.422	0.931	0.350	7.300
C_{15}	2.996	3.487	1.614	0.350	8.447
C_{16}	2.118	2.856	1.710	0.350	7.034
C_{17}	1.735	4.676	1.773	0.350	8.534
C_{18}	1.626	4.821	1.903	0.350	8.700
C_{19}	1.188	2.892	1.058	0.350	5.488
C_{20}	0.941	0.161	0.346	0.350	1.798
C_{21}	1.443	0.577	2.020	0.350	4.390
total	24.386	36.314	13.442	3.500	77.642

evaporated during the liquid chromatographic separation. This loss influences the relative proportion of the saturates and aromatics, and thus the masses of saturates and aromatics in the oil. This places doubt on the accuracy of the original oil's composition. Therefore, the ability to model oil fate is controlled by the capability of the analytical techniques to yield accurate composition information about the oil.

Open column chromatography and gas chromatography seem satisfactory, but high accuracy is not expected, because of the loss of volatiles by evaporation during the separation and analyses of the crude oils. Therefore, the most accurate results are obtained for oils which are so weathered that there are few volatile hydrocarbons remaining. The analytical scheme used here is believed to be the best that is currently available. It provides sufficient information about the oil composition to use the matrix methods.

6.2 Evaporation

Evaporation is an important weathering process from the viewpoint of the mass lost by the bulk oil. The compounds preferentially removed are the volatile, low molecular weight hydrocarbons.

Two experimental methods were used for evaporation. The first technique was gas stripping. It was found to be best for the evaporation of oils which contain a significant amount of low boiling, volatile compounds (C_5 to C_{15} hydrocarbons), and only a small quantity of asphaltenes that give some crude oils their high viscosity. If the crude oil is too viscous, there is a high resistance to the flow of air through the oil. Gas stripping is a useful method to obtain an evaporative exposure Q_E of about 50000 in a

reasonable time which corresponds to a rate of 5000 per day. The maximum flowrate of air possible is about 1.0 L/min. Liquid entrainment will occur at higher flowrates. This system can be modified to allow for the collecting of the stripped hydrocarbons during the evaporation run by using traps which are cooled with liquid nitrogen. The efficiency which can be achieved with two nitrogen traps is approximately 90%. In this case, the maximum possible air flowrate is between 450 and 500 mL/min before the trap efficiency decreases.

The gas stripping method allows for the direct measurement of the total air volume which passed through a known mass and volume of oil. From the measurements of the mass and volume of the oil, the density, the air-to-oil volume ratio (Q_E) and the extent of weathering (the volume and mass fraction evaporated, F_V and F_M) can be calculated for the weathered oils. Moreover, samples of weathered oil can be taken periodically for analyses at different Q_E values.

However, the gas stripping apparatus is not satisfactory for dense and viscous crude oils such as California Crude API 15 oil. Therefore, an alternative method of evaporation is preferable, namely the rotating mesh disk apparatus. This method can achieve high Q_E values within days because of the high air flowrate and small volume of oil used. Q_E less than 5000 cannot be measured accurately because it is within the error margin. The evaporative exposure rate is about 100000 ± 5000 per day which shows that the rotating mesh disk method is about 20 times faster than gas stripping.

To take samples of weathered oil for analyses, the oil must be extracted from the polyester mesh medium with n-pentane. Therefore, for a fixed number of samples to be taken, it is necessary to prepare an equal or greater number of mesh disk-oil samples for

the evaporation experiment. Clearly, reliable data on the extent of oil evaporation can be obtained, but the results are specific to each oil and cannot be generalized.

To further accelerate the evaporation process, thin-film tray evaporation can be used as described by Stiver and Mackay (1984). The rate of exposure which was reached by tray evaporation was a Q_E of 340 per minute or about 500000 per day. This technique is about 100 times faster than gas stripping, and 5 times the rotating mesh disk method.

The gas stripping method is satisfactory for nonviscous crude oils, and for obtaining a Q_E to 50000 in a reasonable time. However, if the crude oil is highly viscous, and a Q_E greater than 50000 is desired, it is preferable to use the rotating mesh disk method.

6.3 Dissolution

When crude oils are subjected to dissolution, the fraction which is dissolved is negligible from the viewpoint of bulk behaviour. However, it is not negligible when groundwater contamination or toxicity to aquatic and marine organisms is considered. The portion of oil which dissolved in water is still susceptible to evaporation because it is not only water-soluble, but it is also likely to be volatile. Therefore, the dissolved hydrocarbons are removed eventually from solution.

The experimental method for the dissolution of crude oils consisted of known volumes of water being pumped through oil which has been plated onto a solid support (i.e. Chromosorb). The generator column method has been reviewed and discussed for pure compounds (Billington et al., 1988) and complex systems such as crude oils (Shiu

et al., 1988). Aqueous samples were collected at intervals, and the dissolved hydrocarbon concentrations determined by purge-and-trap gas chromatography as a function of the water-to-oil volume ratio, Q_D. The dissolution rate is a Q_D of about 2100 per day.

The generator column method proved satisfactory for measuring the decreasing concentration of dissolved hydrocarbons when the oil is exposed to increasing volumes of water. However, it is difficult to measure the changing composition of the oil. Unlike, the evaporation techniques which enable the sampling of weathered oil for composition analyses without too much disruption to the system, the generator column run has to be discontinued at the dissolution exposure rate desired, and the residual oil in the column has to be extracted with solvent before it can be subjected to analyses to determine its composition.

It can be observed that the dissolution process causes a large decrease in the solubility of oil. For example, dissolution reduced the solubility of the synthetic oil from 119 mg/L to 2.4 mg/L in freshwater after an exposure Q_D of 10000.

The experimental data for the synthetic oil exposed to Q_D of 4100 and 10000 are given in Table 6.6. The total amount of oil lost after each Q_D appears to be too high for only dissolution to have occurred. Loss of the hydrocarbons occurred by evaporation during the extraction from the generator column and open column chromatographic separation of the oil. This resulted in an unknown exposure to evaporation. Therefore, care must be taken when interpreting which fraction of the oil was lost by evaporation or dissolution.

The generator column method is useful for determining the change in solubility

of the oil as it is exposed to increasing volumes of water. It is not effective for obtaining oil samples weathered only by dissolution because they also become subject to evaporation.

6.4 Modelling

The first two objectives of the modelling effort were accomplished. Laboratory experiments in which known amounts of oil are subjected to controlled conditions of evaporation and dissolution have been conducted. Using the analytical methods discussed earlier, the composition of the original and weathered oils can be characterized in a matrix in which the rows are of common volatility or GC retention time, and the columns of solubility or chemical classes. The amount remaining of each matrix element or pseudocomponent after exposure can be approximated by the transport equation

$$M_i = M_{io} e^{(-H_{Ei}Q_E - H_{Di}Q_D)} \qquad [3.13]$$

and the new matrix amounts can be calculated and the composition of the bulk oil deduced. The final task is to investigate different matrix definitions, that is, different approaches of grouping chemicals into pseudocomponents with the aim of determining the appropriate one from analytical and modelling viewpoints, and the optimal number of elements. The model results must be validated with laboratory and field data before the model can be used for making routine predictions of an oil's changing composition and properties after exposure in the marine environment.

The first matrix method is the " hydrocarbon class" approach which categorizes the oil composition into a two-dimensional matrix in which the rows are of common volatility (elution groups), and the columns of chemical classes. The calculated data for

each evaporative exposure Q_E were generated using the above transport equation and the simple linear correlations for the physical and chemical properties as given by Eastcott et al. (1990). The physical and chemical properties of each pseudocomponent were estimated from properties of compounds which are known to belong in the same group. The accuracy of the assigned values for each pseudocomponent depends upon whether the known compounds are representative of the unidentified ones in the same group which, in turn, affects the ability of the model to predict oil behaviour accurately.

The mathematical model requires as input data the mass percent of the compounds in the parent or original oil, and the values of the exposure parameters Q_E and Q_D, that is, the ratio of the volume of air or water to the initial volume of oil, respectively. The matrix methods are tested for validity by measuring the changes in composition of the synthetic oil when exposed to isolated evaporation and dissolution.

Evaporation

If only evaporation is considered, then the dissolution exposure Q_D is equal to zero The results from the evaporation experiments of the synthetic oil mixture were compared with the data generated using the "hydrocarbon class" approach. The fit of the experimental composition for an evaporative exposure of about 500 is close to the values calculated by the model. The model underestimates the absolute density (i.e. both the initial and final densities) of the synthetic oil. However, the density changes calculated were comparable to those of the experimental values at low Q_E. At higher Q_E, the values generated by the model are higher than the amount of hydrocarbons remaining in the synthetic hydrocarbon mixture after exposure to evaporation. It is possible to

estimate a fitted Q_E which will generate comparable composition from the model with the experimental data. A correction factor for evaporation, f_E, was introduced which is the ratio of the fitted Q_E to the experimental Q_E. This correction factor is applied to equation 3.13 for calculating the mass remaining of each pseudocomponent to account for any deviation from ideality (which was assumed initially), and to include experimental errors. This results in the following equation

$$M_i = M_{io} e^{(-H_{Ei} f_E Q_E - H_{Di} Q_D)}$$ [6.1]

The correction factor for evaporation f_E was determined to be 1.38 with a standard deviation of ± 0.16. The implication is that evaporation appears to proceed about 38% faster than is estimated theoretically. The primary reason is believed to be the magnitude of the activity coefficients of the hydrocarbons in the oil. Table 6.3 gives the experimental composition of the original and weathered synthetic oil. It includes the composition calculated by the "hydrocarbon class" approach with the evaporation correction factor of 1.38 incorporated into the transport equation 3.13. The compositions in the Q_E range between 200 and 110160 were tested. The "hydrocarbon class" approach proved to yield composition data for the synthetic oil which are comparable with the experimental results. Therefore, the model can be applied with more confidence to heavy crude oils such as California Crude API 15 oil. Some experimental and model results for this heavy crude oil are tabulated in Tables 6.4 and 6.5. The compositions at the evaporative exposures of 100000 and 600000 were examined. In these tables, the total masses of oil remaining calculated by the "hydrocarbon class" approach are less than the experimental values by approximately 15 to 20%. To explain the discrepancy,

Table 6.3 Comparison of experimental composition data and model results from the "Hydrocarbon class" approach for the evaporation of the synthetic oil. Note: masses are in grams (g).

Q_E	0	198			1060			17310			110160		
Compound	expt'l	expt'l	calc'd[1]	calc'd[2]	expt'l	calc'd[1]	calc'd[2]	expt'l	calc'd[1]	calc'd[2]	expt'l	calc'd[1]	calc'd[2]
cyclohexane	4.000	3.235	3.489	3.310	1.366	1.927	1.455	0.000	0.000	0.000	0.000	0.000	0.000
methylcyclohexane	4.000	3.562	3.814	3.749	2.341	3.100	2.810	0.000	0.062	0.012	0.000	0.000	0.000
toluene	6.000	5.504	5.824	5.758	4.145	5.120	4.816	0.051	0.448	0.165	0.000	0.000	0.000
n-octane	8.000	7.541	7.786	7.706	6.416	6.922	6.547	0.667	0.750	0.302	0.000	0.000	0.000
p-xylene	5.500	5.266	5.440	5.417	4.770	5.187	5.072	1.375	2.111	1.460	0.000	0.012	0.001
n-propylbenzene	5.100	4.924	5.080	5.072	4.806	4.992	4.950	2.851	3.588	3.134	0.065	0.544	0.230
n-decane	7.000	6.787	6.982	6.975	6.818	6.905	6.869	5.523	5.602	5.142	1.294	1.691	0.983
p-cresol	1.000	0.977	0.999	0.998	1.021	0.993	0.990	0.855	0.884	0.843	0.510	0.457	0.338
benzo[b]thiophene and quinoline	2.000	1.992	2.000	1.999	2.051	1.998	1.997	1.898	1.968	1.955	1.505	1.802	1.731
tridecane	4.000	3.951	4.000	4.000	4.173	3.999	3.998	3.924	3.976	3.967	3.851	3.850	3.794
1-methylnaphthalene	6.000	5.974	6.000	5.999	6.272	5.998	5.997	5.812	5.963	5.949	5.375	5.770	5.683
tetradecane	14.000	13.918	14.000	14.000	14.593	13.998	13.998	13.785	13.975	13.966	13.915	13.843	13.783
acenaphthene	2.000	2.022	2.000	2.000	1.849	2.000	2.000	1.931	1.998	1.998	1.607	1.990	1.986
hexadecane	19.900	20.106	19.900	19.900	20.288	19.900	19.900	19.519	19.897	19.896	19.318	19.881	19.873
pristane	4.000	4.074	4.000	4.000	4.092	4.000	4.000	3.952	4.000	4.000	3.722	3.998	3.998
octadecane	2.000	2.088	2.000	2.000	2.017	2.000	2.000	1.987	2.000	2.000	1.824	2.000	2.000
phenanthrene	2.000	2.264	2.000	2.000	1.807	2.000	2.000	2.149	2.000	2.000	1.697	2.000	1.999
eicosane	2.000	2.187	2.000	2.000	1.884	2.000	2.000	2.079	2.000	2.000	1.701	2.000	2.000
pyrene	1.500	1.848	1.500	1.500	1.578	1.500	1.500	1.872	1.500	1.500	0.925	1.500	1.500
Final mass (g)	100	98.22	98.81	98.38	92.92	94.54	92.90	70.23	72.72	70.29	57.31	61.34	59.90

[1] mass calculated using the "hydrocarbon class" approach.
[2] mass calculated using the "hydrocarbon class" approach with the evaporation factor $f_E = 1.38$.

Table 6.4 Comparison of experimental composition data and model results from the "Hydrocarbon class" approach at an evaporation of $Q_B=100000$ for California Crude API 15 oil Note: masses are in grams (g).

elution group	normal alkanes		branched alkanes		aromatics		polars		total	
	expt'l	calc'd	expt'l	calc'd	expt'l	calc'd	expt'	calc'd	expt'l	calc'd
C_6	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
C_7	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
C_8	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
C_9	0.000	0.003	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.003
C_{10}	0.000	0.182	0.000	0.118	0.000	0.000	0.000	0.000	0.000	0.300
C_{11}	0.000	0.611	0.000	1.157	0.000	0.000	0.000	0.000	0.000	1.768
C_{12}	0.094	0.843	0.079	0.915	0.000	0.000	0.687	0.356	0.860	2.114
C_{13}	0.262	0.874	0.222	3.880	0.000	0.538	0.687	0.448	1.171	5.740
C_{14}	0.449	1.274	0.908	1.869	1.070	1.596	0.687	0.486	3.114	5.225
C_{15}	0.463	0.896	1.044	0.977	2.408	2.276	0.687	0.501	4.602	4.650
C_{16}	0.516	1.282	3.162	3.152	7.690	7.201	0.687	0.507	12.055	12.142
C_{17}	0.383	0.600	3.018	1.266	7.114	3.016	0.687	0.509	11.202	5.391
C_{18}	0.442	0.500	3.116	2.665	6.562	4.687	0.687	0.510	10.807	8.362
C_{19}	0.340	0.325	2.506	1.040	6.348	1.814	0.687	0.510	9.881	3.689
C_{20}	0.206	0.298	0.980	0.000	3.989	0.000	0.687	0.510	5.862	0.808
C_{21}	0.107	0.012	0.000	0.000	29.219	25.214	0.687	0.510	30.013	25.736
total	3.262	7.700	15.03	17.03	64.400	46.342	6.87	4.847	89.567	75.928

Table 6.5 Comparison of experimental composition data and model results from the "Hydrocarbon class" approach at an evaporation of $Q_B=600000$ for California Crude API 15 oil Note: masses are in grams (g).

elution group	normal alkanes		branched alkanes		aromatics		polars		total	
	expt'l	calc'd	expt'l	calc'd	expt'l	calc'd	expt'l	calc'd	expt'l	calc'd
C_6	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
C_7	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
C_8	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
C_9	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
C_{10}	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
C_{11}	0.000	0.042	0.000	0.002	0.000	0.000	0.000	0.000	0.000	0.044
C_{12}	0.000	0.378	0.000	0.103	0.000	0.000	0.687	0.059	0.687	0.540
C_{13}	0.000	0.688	0.000	1.882	0.000	0.273	0.687	0.233	0.687	3.076
C_{14}	0.000	1.171	0.000	1.472	0.000	1.249	0.687	0.384	0.687	4.276
C_{15}	0.221	0.878	0.147	0.903	0.000	2.083	0.687	0.460	1.055	4.324
C_{16}	0.355	1.275	1.618	3.072	5.173	6.975	0.687	0.491	7.833	11.813
C_{17}	0.569	0.599	3.595	1.255	9.141	2.982	0.687	0.503	13.992	5.339
C_{18}	0.441	0.500	2.384	2.657	10.300	4.668	0.687	0.508	13.812	8.333
C_{19}	0.297	0.325	2.424	1.039	7.619	1.812	0.687	0.509	11.027	3.685
C_{20}	1.182	0.298	0.166	0.000	8.034	0.000	0.687	0.509	10.069	0.807
C_{21}	0.000	0.012	0.000	0.000	26.432	25.209	0.687	0.510	27.119	25.731
total	3.065	6.166	10.334	12.385	66.699	45.251	6.870	4.166	86.968	67.968

the accuracy of the original oil's composition should be considered. As mentioned earlier, the analytical approach underestimates the proportion of high molecular weight hydrocarbons. Therefore, California Crude API 15 oil may have a lower portion of volatile, low molecular weight hydrocarbons, which are highly susceptible to evaporation, than its measured composition illustrated in Appendix D.

Dissolution

To consider the dissolution process in isolation, the evaporative exposure Q_E is assigned a value of zero. The experimental data and model results using the "hydrocarbon class" approach are compiled in Table 6.6 for the synthetic oil exposed to Q_D of 4100 and 10000. It was hoped that the dissolution process can be isolated experimentally, and the data used to validate the model. However, evaporation cannot be eliminated completely, and a little exposure to evaporation causes a significant decrease in the mass of the oil. The experimental data appear to correspond to the calculated results for Q_D of 4100 and Q_E of 2330, and Q_D of 10000 and Q_E of 5430.

The second or "solubility" approach groups the compounds into rows according to elution groups as its first matrix dimension. When the composition matrices from the "hydrocarbon class" and "solubility" approaches for the same oil are compared, the total masses of the hydrocarbons in the corresponding rows are equal. The "solubility" approach presents the oil composition with an emphasis on the solubility of the compounds in the oil. The compounds in each elution group are separated further into columns according to mean aqueous solubility (g/m^3) as the second matrix dimension.

Table 6.6 Comparison of experimental composition data and model results from the "Hydrocarbon class" approach at dissolution exposure Q_D of 4100 and 10000 for the synthetic oil. Note: Mass remaining from initial 100 g of oil (g).

Compound	expt'l	expt'l	calc'd[1]	expt'l	calc'd[1]
cyclohexane	4.000	0.386	0.410	0.000	0.020
methylcyclohexane	4.000	1.558	1.810	0.357	0.629
toluene	6.000	0.070	0.871	0.000	0.057
n-octane	8.000	5.798	5.130	3.231	2.838
p-xylene	5.500	0.000	2.104	0.000	0.538
n-propylbenzene	5.100	2.748	3.135	0.000	1.568
n-decane	7.000	7.095	6.714	5.936	6.350
p-cresol	1.000	0.000	0.412	0.000	0.115
benzo[b]thiophene and quinoline	2.000	0.000	1.558	0.000	1.088
tridecane	4.000	4.097	3.996	4.059	3.990
1-methylnaphthalene	6.000	4.061	5.793	0.404	5.508
tetradecane	14.000	13.996	13.995	14.090	13.898
acenaphthene	2.000	1.592	1.981	0.834	1.953
hexadecane	19.900	19.900	19.899	20.422	19.899
pristane	4.000	3.953	4.000	5.805	4.000
octadecane	2.000	2.002	2.000	2.382	2.000
phenanthrene	2.000	2.160	1.997	2.676	1.993
eicosane	2.000	2.215	2.000	2.936	2.000
pyrene	1.500	2.374	1.499	1.730	1.499
Q_D	0	4100	4100	10000	10000
Q_E	0	0	2330	0	5432
Final mass (g)	100.00	74.01	79.30	64.86	69.94

[1]mass calculated using the "hydrocarbon class" approach with the evaporation factor $f_E = 1.38$.

The present analytical methods used do not separate the bulk oil into fractions of common solubility directly, but rather into groups of chemical classes. Therefore, an additional step was incorporated in which the " hydrocarbon class" pseudocomponents have to be rearranged to correspond to mean aqueous solubility based upon the solubility of the individual pseudocomponents, giving a different set of pseudocomponents. The actual number of pseudocomponents is higher than that used in the "hydrocarbon class" approach, but the "operable" number is much less. These operable pseudocomponents are clustered along the main diagonal of the matrix.

The evaporation correction factor f_E deduced for the "solubility" approach is 1.32 ± 0.36. The difference between the correction factors for evaporation in the "hydrocarbon class" and "solubility" approaches may be caused by the difference in the regression equations for the physical-chemical properties used in each approach. Table 6.7 gives some experimental data and model results using the "solubility" approach with the evaporation correction factor of 1.32.

The number of pseudocomponents involved in both matrix methods is manageable which makes them feasible for predicting the behaviour of oil. However, the "hydrocarbon class" approach is a better method of characterizing the composition of crude oils than the "solubility" approach based upon present analytical abilities to separate the oil into compounds having common physical and chemical properties. In the "hydrocarbon class" approach, open column chromatography separates an oil directly into fraction of different chemical classes, but there are no current analytical methods which give semi-preparative fractions of common solubility. Therefore, the pseudocomponents in the "hydrocarbon class" approach have to be grouped into solubility

Table 6.7 Comparison of experimental composition data and model results from the "Solubility" approach for the evaporation of the synthetic oil. Note: masses are in grams (g).

Q_R	0	198			1060			17310			110160		
Compound	expt'l	expt'l	calc'd¹	calc'd²	expt'l	calc'd¹	calc'd²	expt'l	calc'd¹	calc'd²	expt'l	calc'd¹	calc'd²
cyclohexane	4.000	3.235	3.650	3.545	1.366	2.452	2.094	0.000	0.001	0.000	0.000	0.000	0.000
methylcyclohexane	4.000	3.562	3.874	3.834	2.341	3.369	3.188	0.000	0.242	0.078	0.000	0.000	0.000
toluene	6.000	5.504	5.810	5.571	4.145	5.054	4.782	0.051	0.362	0.148	0.000	0.000	0.000
n-octane	8.000	7.541	7.747	7.668	6.416	6.739	6.376	0.667	0.483	0.197	0.000	0.000	0.000
p-xylene	5.500	5.266	5.439	5.420	4.770	5.182	5.084	1.375	2.078	1.522	0.000	0.011	0.002
n-propylbenzene	5.100	4.924	5.081	5.074	4.806	4.997	4.964	2.851	3.650	3.279	0.065	0.607	0.307
n-decane	7.000	6.787	6.973	6.965	6.818	6.858	6.813	5.523	5.010	4.501	1.294	0.833	0.421
p-cresol	1.000	0.977	0.999	0.998	1.021	0.993	0.991	0.855	0.892	0.860	0.510	0.484	0.383
benzo[b]thiophene and quinoline	2.000	1.992	2.000	2.000	2.051	1.998	1.998	1.898	1.974	1.966	1.505	1.840	1.792
tridecane	4.000	3.951	3.999	3.999	4.173	3.997	3.996	3.924	3.948	3.932	3.851	3.681	3.584
1-methylnaphthalene	6.000	5.974	6.000	6.000	6.272	5.998	5.998	5.812	5.974	5.965	5.375	5.835	5.783
tetradecane	14.000	13.918	13.999	13.999	14.593	13.996	13.995	13.785	13.939	13.919	13.915	13.614	13.492
acenaphthene	2.000	2.022	2.000	2.000	1.849	2.000	2.000	1.931	1.999	1.999	1.607	1.994	1.992
hexadecane	19.900	20.106	19.900	19.900	20.288	19.899	19.899	19.519	19.890	19.887	19.318	19.838	19.818
pristane	4.000	4.074	4.000	4.000	4.092	4.000	4.000	3.952	4.000	4.000	3.722	3.999	3.998
octadecane	2.000	2.088	2.000	2.000	2.017	2.000	2.000	1.987	2.000	2.000	1.824	1.999	1.999
phenanthrene	2.000	2.264	2.000	2.000	1.807	2.000	2.000	2.149	2.000	2.000	1.697	2.000	2.000
eicosane	2.000	2.187	2.000	2.000	1.884	2.000	2.000	2.079	2.000	2.000	1.701	2.000	2.000
pyrene	1.500	1.848	1.500	1.500	1.578	1.500	1.500	1.872	1.500	1.500	0.925	1.500	1.500
Final mass (g)	100	98.22	98.97	98.47	92.92	95.03	93.68	70.23	71.94	69.77	57.31	60.23	59.07

[1] mass calculated using the "solubility" approach.
[2] mass calculated using the "solubility" approach with the evaporation factor $f_E = 1.32$.

classes for use in the "solubility" approach.

From a modelling viewpoint, both the "hydrocarbon class" and "solubility" approaches give composition results which approximate those obtained from the laboratory experiments. Conceptually, the "solubility" approach is more difficult to understand. Some of the pseudocomponents in the matrix do not exist in practice, that is, there do not exist any compounds which have high volatility as well negligible solubility in water, or negligible vapour pressure and high water solubility.

The "HPLC" approach has been described earlier, but no experimental data or model results were obtained. Therefore, it is not possible to discuss full results, and develop any conclusions about this modelling approach. The main potential advantage of the "HPLC" approach is that HPLC is a fast and routine analytical method for separating crude oils into class fractions when compared to open column chromatography used in the "hydrocarbon class" approach. It is recommended that the "HPLC" approach be investigated as a possible method for modelling oil behaviour. It will be necessary to perform exploratory experiments with known hydrocarbons to elucidate the different chemical classes which result from HPLC separation of crude oils, and assign physical and chemical properties to the pseudocomponents.

In conclusion, the evaporation process can be well-characterized. The transport equation gives a good approximation of the changing composition in crude oils as they are exposed to evaporation. For the dissolution process, the approximation given by the transport equation is less certain.

The synthetic oil was valuable in testing and validating the models. Since the physical and chemical properties and chemical structure of the hydrocarbons which are

present in the synthetic oil are known, it is easy to categorize the hydrocarbons into elution groups, and chemical or solubility classes. The "hydrocarbon class" approach is the preferred matrix method from analytical and modelling viewpoints.

The matrix method, which estimates the changes in mass of the chemicals in an oil subject to known exposure of evaporation and dissolution, has been validated. The desired aim is now to use the model to predict the effect of the weathering processes on bulk oil properties such as density, viscosity, vapour pressure and aqueous solubility. It should be possible to estimate the changing properties of the bulk oil from the magnitude of the pseudocomponents and the properties assigned to each of them.

Densities

A concern of heavy crude oils and residual fuels, which have densities exceeding 900 kg/m^3, is that they will increase in density to the extent that they can become denser than seawater and subject to sinking. This sinking phenomenon may have a profound effect on the aquatic and marine organisms. Therefore, it is desirable to determine under which conditions the oils may become denser than seawater. Presently, the model underestimates the absolute densities, that is, the initial and final densities of the bulk oil. For example, the experimental density of fresh California Crude API 15 oil was 968 kg/m^3 compared to 914 kg/m^3 calculated by the matrix method. In order to have a better fit between the experimental and model results, the density or molar volume of each pseudocomponent must be reassigned with a higher or lower value, respectively. However, these changes will alter the composition matrix because the calculation of the mass remaining of each pseudocomponent depends on its properties.

The discrepancy between the experimental and calculated densities suggests that at least some of the densities used in the matrix are in error. The correct density to use in this context is that derived from the partial molar volume (PMV), not the pure component molar volume. There is considerable doubt about the magnitude of these PMVs, especially for the solid hydrocarbons. To establish them would require extensive and accurate data on the densities of mixtures, preferably synthetic mixtures.

It is concluded that at present the matrix method is not well suited for estimating oil densities, nor probably is it likely to be accurate for viscosities. The preferred method is a simple experimental determination of density as a function of weathering with direct empirical regression of the results. This simpler approach is more reliable and accurate.

6.5 Long-term Weathering of Heavy Crude Oils

When crude oils and petroleum products are spilled in the marine environment, they are subject to weathering processes, they become denser and more viscous, and some may form water-in-oil emulsions or mousses, and may ultimately form tar balls. The tar balls may persist on the sea water surface, become stranded on shore, or sink and become incorporated into the bottom sediments. Therefore, as indicated earlier, there is a need to predict the long-term behaviour of oils because they can drift appreciable distances from the source of the spill.

The heavy crude oils were observed for the susceptibility to water-in-oil emulsion and tar ball formation in the relatively simple laboratory system. The thin slick of heavy crude oil was exposed simultaneously to evaporation and dissolution on a water surface

in a cylindrical container. Tl : water was circulated by a magnetic stirrer. This laboratory system has many ex; rimental limitations for observing oil behaviour.

When the oil was releas 1 on the water, spreading occurred. In an attempt to prevent the oil from colliding ; d adhering to the sides of the container, a magnetic stirrer was used to keep the oi in the centre. This approach was not very effective because the oil continued to spr ad outward to the sides.

A side effect of the stirr g was the formation of a vortex in the water column. The vortex drew the oil slowly wards the stirrer bar into a inverted cone-shaped mass. Near the point of impact betwe the oil mass and the stirrer bar, the oil was flung out radially into the surrounding ater to form of oil globules. If the oil is fairly unweathered, the oil floated to e water surface and adhered with the remaining mass. For a weathered oil, the oil glot les may remained in the water column if they are more dense than the water. This phe omenon is illustrated in Figure 6.1.

Microbial degradation a; eared to have occurred in the later stage of weathering since sterile conditions were no established. The water column became cloudy, and the underside of the oil layer turne from a dark to a light brown.

The system devised and sted here was partially successful in that it did enable the conditions of an oil sampl to be observed over a period of months. A major difficulty was that the oil tend to be in one of two conditions. Either it remained relatively stagnant on the watei surface exhibiting negligible weathering, or it became attached to the vessel surface or he impeller. Neither of these conditions simulates the events experienced by an oil m ss on a turbulent water surface where it is subject to repeated deformation, sinking, d exposure of new surfaces to the atmosphere and the

water. Under the conditions investigated, a thin crust appears to form on the oil surface which is sufficiently robust that it prevents diffusion to or from the mass of the oil.

It is concluded that the system devised here is only partly successful and an improved version should be sought in which there is greater turbulence. Unfortunately, it is not easy to conceive of such a system which will be reliable enough to operate unattended for periods of months.
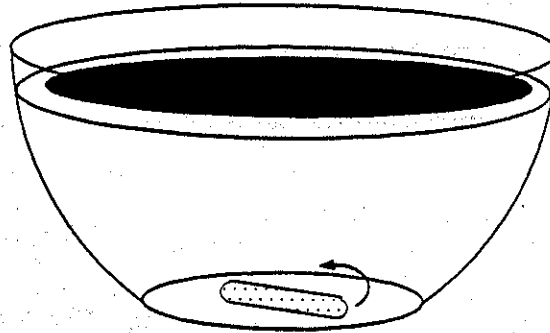
The oil mass spread out towards the sides.
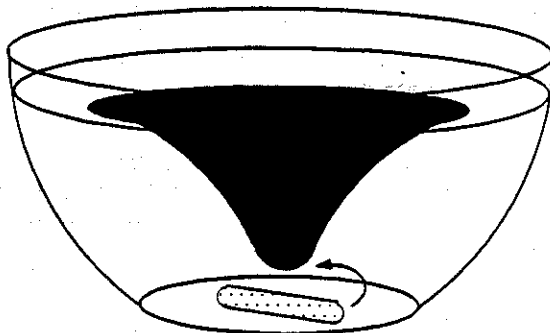
The formation of a vortex caused the oil to be drawn into the water column.
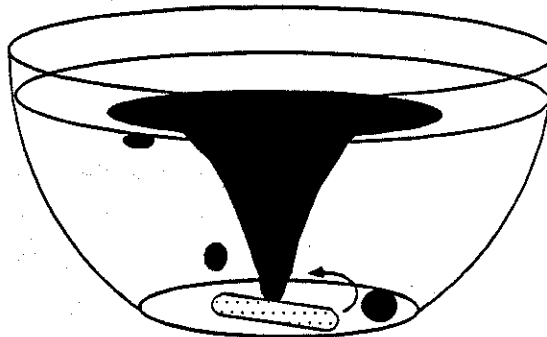
Oil droplets detached from the bulk mass and were flung radially into the water column.

Figure 6.1 The fate of California Crude API 15 oil in the long-term weathering system.

7.0 CONCLUSIONS

- The combination of open column liquid chromatography and gas chromatography is believed to be the best analytical scheme currently available for hydrocarbons in this context. It provides sufficient information for expressing the composition of crude oils in terms of matrix elements or pseudocomponents.

- The gas stripping method is satisfactory for nonviscous crude oils and for obtaining an evaporative exposure Q_E of 50000. For highly viscous crude oils, and a Q_E greater than 50000, the rotating mesh disk method is preferred.

- The generator column method is useful in determining the change in solubility of oil exposed to the dissolution process. It is not effective for obtaining oil samples weathered by only dissolution because they become subject to much greater composition changes as a result of evaporation.

- The evaporation process can be well-characterized. The transport equation gives a satisfactory estimation of the changing composition of crude oils as they are exposed to evaporation. For the dissolution process, the reliability of the transport equation is less certain because of the unavoidable presence of some evaporation.

- The preferred matrix method by which the hydrocarbon mixture can be classified according to its solubility characteristics is the "hydrocarbon class" approach from analytical and modelling viewpoints.

- The synthetic oil, in which the physical-chemical properties, chemical structure and amount of the hydrocarbons are known, is valuable for testing and validating the matrix methods. The use of the synthetic oil makes the theory and functioning of the model easier to understand before applying it to a complex crude oil system.

- The matrix method is not, in its present form, suitable for estimating the changes in oil density and viscosity which arise from long term weathering. Use of a simpler direct empirical regression of experimental data is recommended.

- An experimental system has been devised and tested for exposing oil to the atmosphere on a moving water surface for periods of months. The method is regarded as being only partly successful because turbulent sea-surface conditions are not well simulated.

8.0 RECOMMENDATIONS

- It is recommended that the analytical scheme and the "hydrocarbon class" approach be used for obtaining data on the oil's changing composition in the marine environment. In understanding the fate of crude oils and petroleum products, the appropriate remedial measures can be taken.

- The "HPLC" approach should be investigated as a possible method for modelling oil behaviour. HPLC is a fast and routine analytical technique for separating the oil into class group-type fractions.

- If it is desired to apply the matrix method for the estimation of oil density and viscosity, these properties should be measured first for synthetic oil mixtures to establish partial molar volumes, with subsequent application to the more complex crude oils.

- It is suggested that further novel methods be sought of exposing oil to evaporation and dissolution on a water surface, in an attempt to simulate the long term weathering of crude oils.

NOMENCLATURE

A spill area (m^2)

C^S water solubility (mol/m^3)

f_D dissolution correction factor

f_E evaporation correction factor

F fugacity ratio

G_D saturated water flowrate (m^3/h)

G_E saturated air flowrate (m^3/h)

H Henry's Law constant ($Pa \cdot m^3/mol$)

H_{Ei} dimensionless water-oil partition coefficient of component i

H_{Ei} dimensionless air-oil partition coefficient of component i

K overall mass transfer coefficient (m/s)

k_D mass transfer coefficient for dissolution (m/h)

k_E mass transfer coefficient for evaporation (m/h)

K_{OW} octanol-water partition coefficient

M_i amount of component i (moles)

M_{io} initial amount of component i (moles)

N elution group number

P^S vapour pressure (Pa)

Q_D dissolution exposure

Q_E evaporative exposure

R gas constant ($8.314 \ Pa \cdot m^3/mol \cdot K$)

ΔS entropy of fusion ($J/mol \cdot K$)

t time of exposure (s)

T system temperature (K)

T_M normal melting point temperature (K)

v molar volume (m^3/mol)

V oil volume (m^3)

V_O initial volume of oil (m^3)

x mole fraction

subscript

D	dissolution
E	evaporation
i	ith component
L	liquid
M	melting point
n	number of carbon in a normal alkane
o	initial condition
S	solid

superscript

S	saturation

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APPENDIX A

Physical-chemical Properties of Matrix Elements

Table A.1 Physical-chemical properties of matrix elements for the "Hydrocarbon class" approach

W: MOLECULAR MASS (GRAMS PER MOLE)

elution group	normal alkanes	branched alkanes	aromatics	polars
C_6	86.17	86.17	78.11	73.11
C_7	100.20	100.20	86.45	81.45
C_8	114.22	114.22	94.79	89.79
C_9	128.25	128.25	103.14	98.14
C_{10}	142.28	142.28	111.48	106.48
C_{11}	156.30	156.30	119.82	114.82
C_{12}	170.33	170.33	128.16	123.16
C_{13}	184.35	184.35	136.51	131.51
C_{14}	198.38	198.38	144.85	139.85
C_{15}	212.41	212.41	153.19	148.19
C_{16}	226.43	226.43	161.53	156.53
C_{17}	240.46	240.46	169.88	164.88
C_{18}	254.48	254.48	178.22	173.22
C_{19}	268.51	268.51	186.56	181.56
C_{20}	282.54	282.54	194.91	189.91
C_{21}	296.56	296.56	203.25	198.25

D: DENSITY (KILOGRAMS PER CUBIC METRES)

elution group	normal alkanes	branched alkanes	aromatics	polars
C_6	682	682	779	779
C_7	690	690	812	812
C_8	698	698	845	845
C_9	706	706	878	878
C_{10}	714	714	911	911
C_{11}	722	722	944	944
C_{12}	730	730	977	977
C_{13}	738	738	1010	1010
C_{14}	746	746	1043	1043
C_{15}	754	754	1076	1076
C_{16}	762	762	1109	1109
C_{17}	770	770	1142	1142
C_{18}	778	778	1175	1175
C_{19}	786	786	1208	1208
C_{20}	794	794	1241	1241
C_{21}	802	802	1274	1274

Table A.1 Physical-chemical properties of matrix elements for the "Hydrocarbon class" approach

P: VAPOUR PRESSURE (PASCALS)

elution group	normal alkanes	branched alkanes	aromatics	polars
C_6	2.68E+04	3.80E+04	2.67E+04	2.67E+04
C_7	7.45E+03	1.18E+04	9.40E+03	9.40E+03
C_8	2.07E+03	3.65E+03	3.31E+03	3.31E+03
C_9	5.76E+02	1.13E+03	1.17E+03	1.17E+03
C_{10}	1.60E+02	3.50E+02	4.11E+02	4.11E+02
C_{11}	4.45E+01	1.08E+02	1.45E+02	1.45E+02
C_{12}	1.24E+01	3.36E+01	5.11E+01	5.11E+01
C_{13}	3.44E+00	1.04E+01	1.80E+01	1.80E+01
C_{14}	9.55E-01	3.22E+00	6.34E+00	6.34E+00
C_{15}	2.66E-01	9.98E-01	2.23E+00	2.23E+00
C_{16}	7.38E-02	3.09E-01	7.87E-01	7.87E-01
C_{17}	2.05E-02	9.58E-02	2.77E-01	2.77E-01
C_{18}	5.70E-03	2.97E-02	9.78E-02	9.78E-02
C_{19}	1.59E-03	9.19E-03	3.44E-02	3.44E-02
C_{20}	4.41E-04	2.85E-03	1.21E-02	1.21E-02
C_{21}	1.23E-04	8.81E-04	4.28E-03	4.28E-03

S: WATER SOLUBILITY (GRAMS PER CUBIC METRE)

elution group	normal alkanes	branched alkanes	aromatics	polars
C_6	8.08E+00	3.13E+01	9.22E+02	3.45E+03
C_7	2.55E+00	9.91E+00	5.27E+02	1.99E+03
C_8	7.90E-01	3.07E+00	2.98E+02	1.13E+03
C_9	2.41E-01	9.40E-01	1.68E+02	6.38E+02
C_{10}	7.26E-02	2.84E-01	9.36E+01	3.58E+02
C_{11}	2.17E-02	8.49E-02	5.19E+01	1.99E+02
C_{12}	6.42E-03	2.52E-02	2.87E+01	1.10E+02
C_{13}	1.89E-03	7.42E-03	1.58E+01	6.08E+01
C_{14}	5.51E-04	2.18E-03	8.65E+00	3.34E+01
C_{15}	1.60E-04	6.34E-04	4.72E+00	1.83E+01
C_{16}	4.64E-05	1.84E-04	2.57E+00	9.97E+00
C_{17}	1.34E-05	5.32E-05	1.40E+00	5.42E+00
C_{18}	3.85E-06	1.53E-05	7.57E-01	2.94E+00
C_{19}	1.10E-06	4.41E-06	4.09E-01	1.59E+00
C_{20}	3.16E-07	1.26E-06	2.21E-01	8.60E-01
C_{21}	9.00E-08	3.61E-07	1.19E-01	4.64E-01

Table A.1 Physical-chemical properties of matrix elements for the "Hydrocarbon class" approach

BB: MOLAR VOLUME (CUBIC CENTIMETRE PER MOLE)

elution group	normal alkanes	branched alkanes	aromatics	polars
C_6	126.35	126.35	100.27	93.85
C_7	145.21	145.21	106.47	100.31
C_8	163.64	163.64	112.18	106.26
C_9	181.66	181.66	117.47	111.17
C_{10}	199.27	199.27	122.37	116.88
C_{11}	216.84	216.84	126.93	121.63
C_{12}	233.33	233.33	131.18	126.06
C_{13}	249.80	249.80	135.16	130.02
C_{14}	265.92	265.92	138.88	134.08
C_{15}	281.71	281.71	142.37	137.72
C_{16}	297.15	297.15	145.66	141.15
C_{17}	312.28	312.28	147.75	144.38
C_{18}	327.10	327.10	151.68	147.42
C_{19}	341.62	341.62	154.44	150.03
C_{20}	355.84	355.84	157.06	153.03
C_{21}	369.78	369.78	159.54	155.61

C: WATER SOLUBILITY (MOLES PER CUBIC METRE)

elution group	normal alkanes	branched alkanes	aromatics	polars
C_6	9.23E-02	3.63E-01	1.18E-01	4.72E+01
C_7	2.55E-02	9.89E-02	6.10E+00	2.44E+01
C_8	6.92E-03	2.69E-02	3.15E+00	1.26E+01
C_9	1.88E-03	7.33E-03	1.63E+00	6.50E+00
C_{10}	5.11E-04	2.00E-03	8.39E-01	3.36E+00
C_{11}	1.39E-04	5.43E-04	4.34E-01	1.73E+00
C_{12}	3.77E-05	1.48E-04	2.24E-01	8.95E-01
C_{13}	1.02E-05	4.03E-05	1.16E-01	4.62E-01
C_{14}	2.78E-06	1.10E-05	3.97E-02	2.39E-01
C_{15}	7.55E-07	2.99E-06	3.08E-02	1.23E-01
C_{16}	2.05E-07	8.13E-07	1.59E-02	6.37E-02
C_{17}	5.57E-08	2.21E-07	8.22E-03	3.29E-02
C_{18}	1.51E-08	6.03E-08	4.25E-03	1.70E-02
C_{19}	4.11E-09	1.64E-08	2.19E-03	8.77E-03
C_{20}	1.12E-09	4.47E-09	1.13E-03	4.53E-03
C_{21}	3.03E-10	1.22E-09	5.85E-04	2.34E-03

Table A.1 Physical-chemical properties of matrix elements for the "Hydrocarbon class" approach

He: AIR-TO-WATER PARTITION COEFFICENT (DIMENSIONLESS)

elution group	normal alkanes	branched alkanes	aromatics	polars
C_6	1.37E-03	1.94E-03	1.08E-03	1.01E-03
C_7	4.37E-04	6.90E-04	4.04E-03	3.80E-04
C_8	1.37E-04	2.41E-04	1.50E-04	1.42E-04
C_9	4.22E-05	8.28E-05	5.53E-05	5.26E-05
C_{10}	1.29E-05	2.81E-05	2.03E-05	1.94E-05
C_{11}	3.89E-06	9.47E-06	7.42E-06	7.11E-06
C_{12}	1.16E-06	3.16E-06	2.70E-06	2.60E-06
C_{13}	3.46E-07	1.05E-06	9.81E-07	9.45E-07
C_{14}	1.03E-07	3.46E-07	3.55E-07	3.43E-07
C_{15}	3.02E-08	1.13E-07	1.28E-07	1.24E-07
C_{16}	8.85E-09	3.71E-08	4.63E-08	4.48E-08
C_{17}	2.59E-09	1.21E-08	1.67E-08	1.62E-08
C_{18}	7.53E-10	3.91E-09	5.98E-09	5.82E-09
C_{19}	2.19E-10	1.27E-09	2.15E-09	2.09E-09
C_{20}	6.33E-11	4.09E-10	7.69E-10	7.49E-10
C_{21}	1.83E-11	1.32E-10	2.75E-10	2.69E-10

Hd: WATER-TO-OIL PARTITION COEFFICIENT (DIMENSIONLESS)

elution group	normal alkanes	branched alkanes	aromatics	polars
C_6	1.18E-05	4.59E-05	1.18E-03	4.43E-03
C_7	3.70E-06	1.44E-05	6.49E-04	2.45E-03
C_8	1.13E-06	4.40E-06	3.53E-04	1.34E-03
C_9	3.41E-07	1.33E-06	1.91E-04	7.27E-04
C_{10}	1.02E-07	3.98E-07	1.03E-04	3.92E-04
C_{11}	3.00E-08	1.18E-07	5.50E-05	2.11E-04
C_{12}	8.79E-08	3.45E-08	2.94E-05	1.13E-04
C_{13}	2.56E-09	1.01E-08	1.56E-05	6.02E-05
C_{14}	7.39E-10	2.92E-09	8.29E-06	3.20E-05
C_{15}	2.13E-10	8.41E-10	4.39E-06	1.70E-05
C_{16}	6.10E-11	2.42E-10	2.32E-06	8.99E-06
C_{17}	1.74E-11	6.91E-11	1.22E-06	4.75E-06
C_{18}	4.95E-12	1.97E-11	6.44E-06	2.50E-06
C_{19}	1.40E-12	5.60E-12	3.39E-07	1.32E-06
C_{20}	3.97E-13	1.59E-12	1.78E-07	6.93E-07
C_{21}	1.12E-13	4.50E-13	9.33E-08	3.64E-07

APPENDIX B

Computer Programs

B.1 Computer program listing for the "Hydrocarbon class" approach and the data file for the synthetic oil

```
10 'MATRIX METHOD--"HYDROCARBON CLASS" APPROACH
20 '
30 CLASS=4
40 COMP=21!
50 'DIMENSION THE ARRAYS
60 COMPI=6!:COMPF=21!:COMPU=COMPF-COMPI+1
70 DIM P(COMP,CLASS), S(COMP,CLASS), C(COMP,CLASS), Z(COMP+1,CLASS+1),
B(COMP+1,CLASS+1),BB(COMP+1,CLASS+1), W(COMP,CLASS),
ZF(COMP+1,CLASS+1), ZW(COMP+1,CLASS+1), HE(COMP+1,CLASS+1)
80 DIM HD(COMP+1,CLASS+1),D(COMP+1,CLASS+1),K(COMP+1,CLASS+1)
,HL(COMP+1,CLASS+1)
,V(COMP+1,CLASS+1),VW(COMP+1,CLASS+1),ZL(COMP+1,CLASS+1)
90 CLS
100 GOSUB 1800              'READ THE DATA FILE FOR COMPOSITIONS
110 '
120 'CALCULATE PROPERTIES
130 '
140    R=8.314
150    TC=25!
160    TK=TC+273.1
170 FOR I=COMPI TO COMPF
180    W(I,1)=I*12.01+2*1.008*(I+1)
190    W(I,2)=W(I,1)
200    W(I,3)=(6+4*(I-6)/6)*12.01+(6+2*(I-6)/6)*1.008
210    W(I,4)=W(I,3)-5
220    P(I,1)=R*TK*(10^(4.37-.556*I))
230    P(I,2)=R*TK*(10^(4.24-.509*I))
240    P(I,3)=R*TK*(10^(3.75-.453*I))
250    P(I,4)=P(I,3)
260    D(I,1)=634!+I*8!
270    D(I,2)=D(I,1)
280    D(I,3)=581!+I*33!
290    D(I,4)=D(I,3)
300    C(I,1)=(10^(2.368-.566*I))
310    C(I,2)=(10^(2.95-.565*I))
320    C(I,3)=(10^(2.794-.287*I))
330    C(I,4)=C(I,3)*4!
340 NEXT I
350 VT=0
360 FOR I=6 TO COMP
370    FOR J=1 TO CLASS
380      V(I,J)=Z(I,J)/D(I,J)  'MASS/DENSITY=VOLUME OF EACH COMPONENT IN CLASS
390      VT=VT+V(I,J)
400    NEXT J
410 NEXT I
420 DT=ZTT/VT  'INITIAL DENSITY OF OIL
430 INPUT "NAME OF OUTPUT FILE =>", NAM2$
440 IF NAM2$="" THEN GOTO 430
450 OPEN NAM2$ FOR OUTPUT AS #2
```

```
460 '
470 'INPUT EXPOSURE CONDITIONS
480 '
490 PRINT #2, "CALCULATION OF THE WEATHERING OF ";OILTYPE$:PRINT #2, " "
500 PRINT " "
510 PRINT "DO YOU WANT TO STORE THE OIL COMPONENT PROPERTIES ON DISK?"
520 INPUT "(Y)ES OR (N)O = >";PRP$
530 IF PRP$="Y" OR PRP$="y" THEN PROP=1:IF PRP$="N" OR PRP$="n" THEN PROP=0
540 PRINT " "
550 PRINT "INPUT EXPOSURE CONDITIONS"
560 INPUT "EVAPORATIVE EXPOSURE Qe = >";QE
570 INPUT "DISSOLUTION EXPOSURE Qd = >";QD
580 PRINT #2, "EVAPORATIVE EXPOSURE Qe          ",QE
590 PRINT #2, "DISSOLUTION EXPOSURE Qd          ",QD
600 PRINT #2, " ":PRINT #2, " "
610 ZWT=0 :VWT=0
620 FOR J = 1 TO CLASS
630   FOR I=6 TO COMP
640 '
650 'CALCULATE THE PARTITION COEFFICIENTS
660 '
670    B(I,J)=W(I,J)/(1000*D(I,J))  'B IS MOLAR VOLUME(CUBIC METRE/MOL)
680    BB(I,J)=B(I,J)*1000000!  'BB IS MOLAR VOLUME(CUBIC CENTIMETRES/MOL)
690 '
700    S(I,J)=C(I,J)*W(I,J)
710    HE(I,J)=P(I,J)/(R*TK)*B(I,J)
720    HD(I,J)=C(I,J)*B(I,J)
730 '
740 'CALCULATE THE REMAINING MASS
750 '
760    QEH=QE*HE(I,J)
770    QDH=QD*HD(I,J)
780    FE=1.38 'CORRECTION FACTOR FOR EVAPORATION
790    ZW(I,J)=Z(I,J)*EXP(-(FE*QEH)-QDH) 'ZW IS MASS REMAINING
800    ZL(I,J)=Z(I,J)-ZW(I,J) 'ZL IS MASS LOST
810    ZWT=ZWT+ZW(I,J)
820    VW(I,J)=ZW(I,J)/D(I,J)
830    VWT=VWT+VW(I,J)
840   NEXT I
850 NEXT J
860 DWT=ZWT/VWT 'FINAL DENSITY OF OIL
870 PRINT #2, " "
880 PRINT #2, "Initial density kg/m3 ";DT
890 PRINT #2, "Final density kg/m3   ";DWT
900 PRINT #2, " "
910 FOR J = 1 TO CLASS
920   FOR I = 6 TO COMP
930    ZF(I,J)=100*ZW(I,J)/ZWT          'ZF IS FINAL MASS PERCENT
940   NEXT I
950 NEXT J
960 '
970 'CALCULATE TOTALS OF ROWS
980 '
990 FOR I=6 TO COMP
```

```
1000    Z(I,CLASS+1)=0
1010    ZW(I,CLASS+1)=0
1020    ZF(I,CLASS+1)=0
1030    ZL(I,CLASS+1)=0
1040    FOR J=1 TO CLASS
1050      Z(I,CLASS+1)=Z(I,CLASS+1)+Z(I,J)
1060      ZW(I,CLASS+1)=ZW(I,CLASS+1)+ZW(I,J)
1070      ZF(I,CLASS+1)=ZF(I,CLASS+1)+ZF(I,J)
1080      ZL(I,CLASS+1)=ZL(I,CLASS+1)+ZL(I,J)
1090    NEXT J
1100  NEXT I
1110 '
1120 'CALCULATE TOTALS OF COLUMNS
1130 '
1140  FOR J=1 TO CLASS+1
1150    Z(COMP+1,J)=0
1160    ZW(COMP+1,J)=0
1170    ZF(COMP+1,J)=0
1180    ZL(COMP+1,J)=0
1190    FOR I=6 TO COMP
1200      Z(COMP+1,J)=Z(COMP+1,J)+Z(I,J)
1210      ZW(COMP+1,J)=ZW(COMP+1,J)+ZW(I,J)
1220      ZF(COMP+1,J)=ZF(COMP+1,J)+ZF(I,J)
1230      ZL(COMP+1,J)=ZL(COMP+1,J)+ZL(I,J)
1240    NEXT I
1250  NEXT J
1260 IF PROP=0 THEN GOTO 1540
1270 '
1280 'PRINT THE PROPERTY AND COMPOSITION ARRAYS
1290 '
1300 PRINT #2, "W : MOLECULAR MASS (GRAMS PER MOLE)"
1310  CODE$="W"
1320  GOSUB 2090
1330 PRINT #2, "P : VAPOUR PRESSURE (PASCALS)"
1340  CODE$="P"
1350  GOSUB 2090
1360 PRINT #2, "S : WATER SOLUBILITY (GRAMS PER CUBIC METRE)"
1370  CODE$="S"
1380  GOSUB 2090
1390 PRINT #2, "C : WATER SOLUBILITY (MOLES PER CUBIC METRE)"
1400  CODE$="C"
1410  GOSUB 2090
1420 PRINT #2, "D : DENSITY (KILOGRAMS PER CUBIC METRE)"
1430  CODE$="D"
1440  GOSUB 2090
1450 PRINT #2, "B : MOLAR VOLUME (CUBIC CENTIMETRES PER MOLE)"
1460  CODE$="BB"
1470  GOSUB 2090
1480 PRINT #2, "He : AIR-TO-OIL PARTITION COEFFICIENT (DIMENSIONLESS)"
1490  CODE$="HE"
1500  GOSUB 2090
1510 PRINT #2, "Hd : WATER-TO-OIL PARTITION COEFFICIENT (DIMENSIONLESS)"
1520  CODE$="HD"
1530  GOSUB 2090
```

```
1540  PRINT #2, "Z :  INITIAL MASS PER 100 G OIL OR PERCENT"
1550  CODE$="Z"
1560  GOSUB 2430
1570  PRINT #2, "ZW :  FINAL MASS PER INITIAL 100 G OIL"
1580  CODE$="ZW"
1590  GOSUB 2430
1600  PRINT #2, "ZF :  FINAL MASS PERCENT"
1610  CODE$="ZF"
1620  GOSUB 2430
1630  PRINT #2, "ZL :  MASS LOST PER INITIAL 100 G OIL"
1640  CODE$="ZL"
1650  GOSUB 2430
1660  '
1670  PRINT " "
1680  INPUT "DO YOU WANT TO ENTER DIFFERENT EXPOSURE CONDITIONS? (Y)ES OR
(N)O = >";CT$
1690  IF CT$="N" OR CT$="n" THEN ANS=1:IF CT$="Y" OR CT$="y" THEN ANS=2
1700  ON ANS GOTO 2820,1710
1710  FOR I= 6 TO COMP
1720    FOR J=1 TO CLASS
1730      Z(I,J)=ZW(I,J)
1740    NEXT J
1750  NEXT I
1760  PROP=0
1770  GOTO 560
1780  CLOSE #2
1790  '
1800  'SUBROUTINE:  READ DATA FILE AND NORMALIZE TO 100
1810  '
1820  INPUT "NAME OF DATA FILE = >", NAM$
1830  IF NAM$="" THEN GOTO 1820
1840  OPEN NAM$ FOR INPUT AS #1
1850  INPUT #1, OILTYPE$
1860  FOR K=6 TO COMPF
1870    INPUT #1, I
1880    FOR J=1 TO CLASS
1890      INPUT #1, Z(I,J)
1900    NEXT J
1910  NEXT K
1920  ZT=0
1930  FOR J=1 TO CLASS
1940    FOR I=6 TO COMP
1950      ZT=ZT+Z(I,J)
1960    NEXT I
1970  NEXT J
1980  ZTT=0
1990  FOR J=1 TO CLASS
2000    FOR I=6 TO COMP
2010      Z(I,J)=Z(I,J)*100/ZT
2020      ZTT=ZTT+Z(I,J)
2030    NEXT I
2040  NEXT J
2050  RETURN
2060  CLOSE #1
```

```
2070  RETURN
2080 '
2090 'SUBROUTINE:  PRINT HEADINGS ON THE PROPERTIES TABLES
2100 '
2110  PRINT #2, "_____ "
2120  PRINT #2, "|          |";
2130 FOR J=1 TO CLASS
2140   PRINT #2, "          |";
2150 NEXT J
2160 PRINT #2, " "
2170 PRINT #2, "|          |";
2180 PRINT #2, " N-ALKANE | BR-ALKANE| AROMATIC |   POLAR  |"
2190 PRINT #2, "|          |";
2200 FOR J=1 TO CLASS
2210   PRINT #2, "          |";
2220 NEXT J
2230 PRINT #2, " "
2240 FOR I=6 TO COMP
2250   PRINT #2, USING "|#####";I;
2260   PRINT #2, "     |";
2270   FOR J=1 TO CLASS
2280     IF CODE$="W" THEN PRINT #2, USING "####.##   |"; W(I,J);: GOTO 2360
2290     IF CODE$="P" THEN PRINT #2, USING "##.##^^^^ |"; P(I,J);: GOTO 2360
2300     IF CODE$="S" THEN PRINT #2, USING "##.##^^^^ |"; S(I,J);: GOTO 2360
2310     IF CODE$="C" THEN PRINT #2, USING "##.##^^^^ |"; C(I,J);: GOTO 2360
2320     IF CODE$="D" THEN PRINT #2, USING "####.##   |"; D(I,J);: GOTO 2360
2330     IF CODE$="BB" THEN PRINT #2, USING "####.##   |"; BB(I,J);: GOTO 2360
2340     IF CODE$="HE" THEN PRINT #2, USING "#.###^^^^ |"; HE(I,J);: GOTO 2360
2350     IF CODE$="HD" THEN PRINT #2, USING "#.###^^^^ |"; HD(I,J);: GOTO 2360
2360   NEXT J
2370   PRINT #2, " "
2380   IF I=COMP THEN PRINT #2,
"|_____|_____|_____|_____|_____|"
2390 NEXT I
2400 PRINT #2, " ":PRINT #2, " "
2410 RETURN
2420 '
2430 'SUBROUTINE:  PRINT HEADINGS ON THE COMPOSITION TABLES
2440 '
2450  PRINT #2, "_____ ,
2460  PRINT #2, "|          |";
2470 FOR J=1 TO CLASS+1
2480   PRINT #2, "          |";
2490 NEXT J
2500 PRINT #2, " "
2510 PRINT #2, "|          |";
2520 PRINT #2, " N-ALKANE | BR-ALKANE| AROMATIC |   POLAR  |   TOTAL  |"
2530 PRINT #2, "|          |";
2540 FOR J=1 TO CLASS +1
2550   PRINT #2, "          |";
2560 NEXT J
2570 PRINT #2, " "
2580 FOR I=6 TO COMP
2590   PRINT #2, USING "|#####";I;
```

```
2600   PRINT #2, "     |";
2610   FOR J=1 TO CLASS+1
2620     IF CODE$="Z" THEN PRINT #2, USING " ####.###  |"; Z(I,J);: GOTO 2660
2630     IF CODE$="ZW" THEN PRINT #2, USING " ####.###  |"; ZW(I,J);: GOTO 2660
2640     IF CODE$="ZF" THEN PRINT #2, USING " ####.###  |"; ZF(I,J);: GOTO 2660
2650     IF CODE$="ZL" THEN PRINT #2, USING "  ###.###  |"; ZL(I,J);: GOTO 2660
2660   NEXT J
2670   PRINT #2, " "
2680   IF I=COMP THEN PRINT #2,
"|_____|_____|_____|_____|_____|_____|_____|"
2690 NEXT I
2700 PRINT #2, "|  TOTAL  |";
2710 I=COMP+1
2720 FOR J=1 TO CLASS+1
2730   IF CODE$="Z" THEN PRINT #2, USING "####.###  |"; Z(I,J);: GOTO 2770
2740   IF CODE$="ZW" THEN PRINT #2, USING "####.###  |"; ZW(I,J);: GOTO 2770
2750   IF CODE$="ZF" THEN PRINT #2, USING "####.###  |"; ZF(I,J);: GOTO 2770
2760   IF CODE$="ZL" THEN PRINT #2, USING "####.###  |"; ZL(I,J);: GOTO 2770
2770 NEXT J
2780 PRINT #2, " "
2790 PRINT #2, "|_____|_____|_____|_____|_____|_____|_____|"
2800 PRINT #2, " ":PRINT #2, " "
2810 RETURN
2820 END


SYNTHETIC OIL
6,0.0,0.0,0.0,0.0
7,0.0,4.0,0.0,0.0
8,8.0,4.0,6.0,0.0
9,0.0,0.0,5.5,0.0
10,7.0,0.0,5.1,0.0
11,0.0,0.0,0.0,1.0
12,0.0,0.0,0.0,0.0
13,4.0,0.0,0.0,2.0
14,14.0,0.0,6.0,0.0
15,0.0,0.0,0.0,0.0
16,19.9,0.0,2.0,0.0
17,0.0,0.0,0.0,0.0
18,2.0,4.0,0.0,0.0
19,0.0,0.0,2.0,0.0
20,2.0,0.0,0.0,0.0
21,0.0,0.0,1.5,0.0
```

B.2 Computer program listing for the "Solubility" approach and the data file for the synthetic oil

```
10 'MATRIX METHOD--"SOLUBILITY" APPROACH
20 '
30 CLASS=10
40 COMP=21!
50 'DIMENSION THE ARRAYS
60 COMPI=6!:COMPF=21!:COMPU=COMPF-COMPI+1
70  DIM P(COMP,CLASS), S(COMP,CLASS), C(COMP+1,CLASS+1), Z(COMP+1,CLASS+1),
        B(COMP+1,CLASS+1),BB(COMP+1,CLASS+1), W(COMP,CLASS),
ZF(COMP+1,CLASS+1), ZW(COMP+1,CLASS+1), HE(COMP+1,CLASS+1)
80 DIM HD(COMP+1,CLASS+1),D(COMP+1,CLASS+1),K(COMP+1,CLASS+1)
,HL(COMP+1,CLASS+1)
,V(COMP+1,CLASS+1),VW(COMP+1,CLASS+1),ZL(COMP+1,CLASS+1)
90 CLS
100  GOSUB 1750            'READ THE DATA FILE FOR COMPOSITIONS
110 '
120 'CALCULATE PROPERTIES
130 '
140    R=8.314
150    TC=25!
160    TK=TC+273.1
170 FOR J=1 TO CLASS
180  FOR I=COMPI TO COMPF
190   W(I,J)=11.18*I+13.78
200   P(I,J)=R*TK*(10^(4.03-.493*I))
210   D(I,J)=608+I*21
220  NEXT I
230 NEXT J
270 FOR I=COMPI TO COMPF
280  FOR J= 1 TO CLASS
290   S(I,J)=10^(3!-J)
300  NEXT J
310 NEXT I
320 VT=0
330 FOR I=6 TO COMP
340 FOR J=1 TO CLASS
350  V(I,J)=Z(I,J)/D(I,J)
360  VT=VT+V(I,J)
370 NEXT J
380 NEXT I
390 DT=ZTT/VT 'INITIAL DENSITY OF OIL
400 INPUT "NAME OF OUTPUT FILE  =>",NAM2$
410 IF NAM2$="" THEN GOTO 400
420 OPEN NAM2$ FOR OUTPUT AS #2
430 '
440 'INPUT EXPOSURE CONDITIONS
450 '
460 PRINT #2, "CALCULATION OF THE WEATHERING OF ";OILTYPE$:PRINT #2, " "
470 PRINT " "
480 PRINT "DO YOU WANT STORE THE OIL COMPONENT PROPERTIES ON DISK?"
```

```
490 INPUT "(Y)ES OR (N)O = > ";PRP$
500 IF PRP$="Y" OR PRP$="y" THEN PROP=1:IF PRP$="N" OR PRP$="n" THEN PROP=O
510 PRINT " "
520 PRINT "INPUT EXPOSURE CONDITIONS"
530 INPUT "EVAPORATIVE EXPOSURE Qe = > ";QE
540 INPUT "DISSOLUTION EXPOSURE Qd = > ";QD
550 PRINT #2, "EVAPORATIVE EXPOSURE Qe          ",QE
560 PRINT #2, "DISSOLUTION EXPOSURE Qd          ",QD
570 PRINT #2, " ":PRINT #2, " "
580  ZWT=0 :VWT=0
590  FOR J = 1 TO CLASS
600   FOR I=6 TO COMP
610 '
620 'CALCULATE THE PARTITION COEFFICIENTS
630 '
640    B(I,J)=W(I,J)/(1000*D(I,J))  'B IS MOLAR VOLUME(CUBIC METRE/MOL)
650    BB(I,J)=B(I,J)*1000000!
660    C(I,J)=S(I,J)/W(I,J)
670    HE(I,J)=P(I,J)/(R*TK)*B(I,J)
680    HD(I,J)=C(I,J)*B(I,J)
690 '
700 'CALCULATE THE REMAINING MASS
710 '
720    QEH=QE*HE(I,J)
730    QDH=QD*HD(I,J)
740    ZW(I,J)=Z(I,J)*EXP(-QEH-QDH) 'ZW IS MASS REMAINING
750    ZL(I,J)=Z(I,J)-ZW(I,J) 'ZL IS MASS LOST
760    ZWT=ZWT+ZW(I,J)
770    VW(I,J)=ZW(I,J)/D(I,J)
780    VWT=VWT+VW(I,J)
790   NEXT I
800  NEXT J
810 DWT=ZWT/VWT 'FINAL OIL DENSITY
820 PRINT #2, " "
830 PRINT #2, "Initial density kg/m3 ";DT
840 PRINT #2, "Final density kg/m3    ";DWT
850 PRINT #2, " "
860 FOR J = 1 TO CLASS
870  FOR I = 6 TO COMP
880   ZF(I,J)=100*ZW(I,J)/ZWT          'ZF IS FINAL MASS PERCENT
890  NEXT I
900 NEXT J
910 '
920 'CALCULATE TOTALS OF ROWS
930 '
940 FOR I=6 TO COMP
950  Z(I,CLASS+1)=0
960  ZW(I,CLASS+1)=0
970  ZF(I,CLASS+1)=0
980  ZL(I,CLASS+1)=0
990  FOR J=1 TO CLASS
1000   Z(I,CLASS+1)=Z(I,CLASS+1)+Z(I,J)
1010   ZW(I,CLASS+1)=ZW(I,CLASS+1)+ZW(I,J)
1020   ZF(I,CLASS+1)=ZF(I,CLASS+1)+ZF(I,J)
```

```
1030    ZL(I,CLASS+1)=ZL(I,CLASS+1)+ZL(I,J)
1040   NEXT J
1050  NEXT I
1060 '
1070 'CALCULATE TOTALS OF COLUMNS
1080 '
1090  FOR J=1 TO CLASS+1
1100   Z(COMP+1,J)=0
1110   ZW(COMP+1,J)=0
1120   ZF(COMP+1,J)=0
1130   ZL(COMP+1,J)=0
1140   FOR I=6 TO COMP
1150    Z(COMP+1,J)=Z(COMP+1,J)+Z(I,J)
1160    ZW(COMP+1,J)=ZW(COMP+1,J)+ZW(I,J)
1170    ZF(COMP+1,J)=ZF(COMP+1,J)+ZF(I,J)
1180    ZL(COMP+1,J)=ZL(COMP+1,J)+ZL(I,J)
1190   NEXT I
1200  NEXT J
1210 IF PROP=0 THEN GOTO 1490
1220 '
1230 'PRINT THE PROPERTY AND COMPOSITION ARRAYS
1240 '
1250 PRINT #2, "W : MOLECULAR MASS (GRAMS PER MOLE)"
1260 CODE$="W"
1270 GOSUB 2040
1280 PRINT #2, "P : VAPOUR PRESSURE (PASCALS)"
1290 CODE$="P"
1300 GOSUB 2040
1310 PRINT #2, "S : WATER SOLUBILITY (GRAMS PER CUBIC METRE)"
1320 CODE$="S"
1330 GOSUB 2040
1340 PRINT #2, "C : WATER SOLUBILITY (MOLES PER CUBIC METRE)"
1350 CODE$="C"
1360 GOSUB 2040
1370 PRINT #2, "D : DENSITY (KILOGRAMS PER CUBIC METRE)"
1380 CODE$="D"
1390 GOSUB 2040
1400 PRINT #2, "BB : MOLAR VOLUME (CUBIC CENTIMETRES PER MOLE)"
1410 CODE$="BB"
1420 GOSUB 2040
1430 PRINT #2, "He : AIR-TO-OIL PARTITION COEFFICIENT (DIMENSIONLESS)"
1440 CODE$="HE"
1450 GOSUB 2040
1460 PRINT #2, "Hd : WATER-TO-OIL PARTITION COEFFICIENT (DIMENSIONLESS)"
1470 CODE$="HD"
1480 GOSUB 2040
1490 PRINT #2, "Z :  INITIAL MASS PER 100 G OIL OR PERCENT"
1500 CODE$="Z"
1510 GOSUB 2410
1520 PRINT #2, "ZW :  FINAL MASS PER INITIAL 100 G OIL"
1530 CODE$="ZW"
1540 GOSUB 2410
1550 PRINT #2, "ZF :  FINAL MASS PERCENT"
1560 CODE$="ZF"
```

```
1570  GOSUB 2410
1580  PRINT #2, "ZL :  MASS LOST PER INITIAL 100 G OIL"
1590  CODE$="ZL"
1600  GOSUB 2410
1610 '
1620 PRINT " "
1630 INPUT "DO YOU WANT TO ENTER DIFFERENT EXPOSURE CONDITIONS? (Y)ES OR
(N)O = > ";CT$
1640 IF CT$="N" OR CT$="n" THEN ANS=1:IF CT$="Y" OR CT$="y" THEN ANS=2
1650 ON ANS GOTO 2830,1660
1660 FOR I= 6 TO COMP
1670  FOR J=1 TO CLASS
1680    Z(I,J)=ZW(I,J)
1690  NEXT J
1700 NEXT I
1710 PROP=0
1720 GOTO 530
1730 CLOSE #2
1740 '
1750 'SUBROUTINE:  READ DATA FILE AND NORMALIZE TO 100
1760 '
1770 INPUT "NAME OF DATA FILE = > ",NAM$
1780 IF NAM$="" GOTO 1760
1790 OPEN NAM$ FOR INPUT AS #1
1800 INPUT #1, OILTYPE$
1810 FOR K=6 TO COMPF
1820  INPUT #1, I
1830  FOR J=1 TO CLASS
1840    INPUT #1, Z(I,J)
1850  NEXT J
1860 NEXT K
1870 ZT=0
1880 FOR J=1 TO CLASS
1890  FOR I=6 TO COMP
1900    ZT=ZT+Z(I,J)
1910  NEXT I
1920 NEXT J
1930 ZTT=0
1940 FOR J=1 TO CLASS
1950  FOR I=6 TO COMP
1960    Z(I,J)=Z(I,J)*100/ZT
1970    ZTT=ZTT+Z(I,J)
1980  NEXT I
1990 NEXT J
2000 RETURN
2010 CLOSE #1
2020  RETURN
2030 '
2040 'SUBROUTINE:  PRINT HEADINGS ON THE PROPERTIES TABLES
2050 '
2060  PRINT #2, "
```

```
2070  PRINT #2, "|      |";
```

APPENDIX C

Gas Chromatograms of Heavy Crude Oils
and Their Saturate and Aromatic Fractions
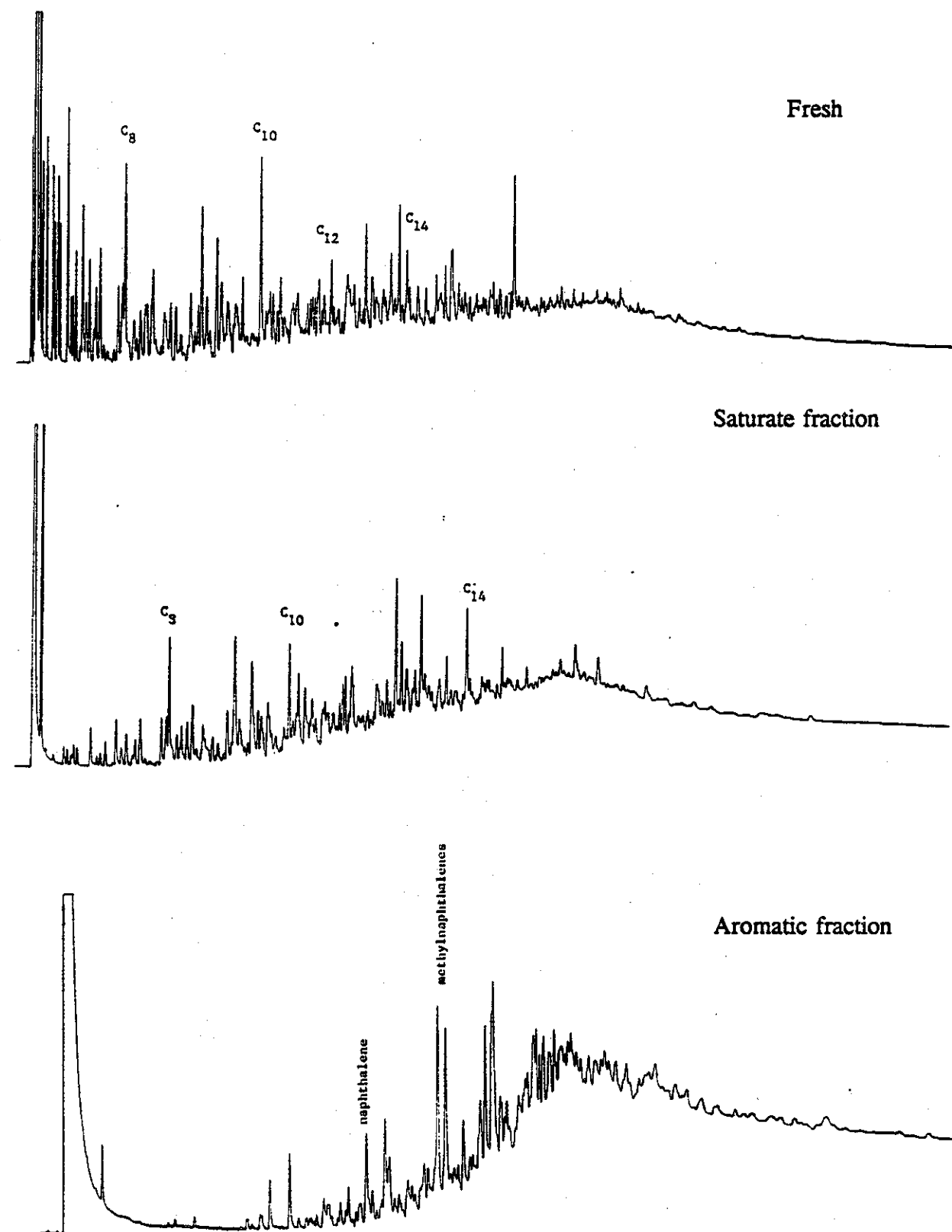
Figure C.1 Gas chromatograms of fresh California Crude API 11 oil and its saturate and aromatic fractions.

```
2080 FOR J=1 TO CLASS
2090  PRINT #2, "        |";
2100 NEXT J
2110 PRINT #2, " "
2120 PRINT #2, "|         |";
2130 FOR J=1 TO CLASS
2140  PRINT #2, USING "    ###  |";J;
2150 NEXT J
2160 PRINT #2, " "
2170 PRINT #2, "|         |";
2180 FOR J=1 TO CLASS
2190  PRINT #2, "        |";
2200 NEXT J
2210 PRINT #2, " "
2220  FOR I=6 TO COMP
2230  PRINT #2, USING "|#####";I;
2240  PRINT #2, "    |";
2250   FOR J=1 TO CLASS
2260     IF CODE$="W" THEN PRINT #2, USING "####.##  |"; W(I,J);: GOTO 2340
2270     IF CODE$="P" THEN PRINT #2, USING "##.##^^^^|"; P(I,J);: GOTO 2340
2280     IF CODE$="S" THEN PRINT #2, USING "##.##^^^^|"; S(I,J);: GOTO 2340
2290     IF CODE$="C" THEN PRINT #2, USING "##.##^^^^|"; C(I,J);: GOTO 2340
2300     IF CODE$="D" THEN PRINT #2, USING "####.##  |"; D(I,J);: GOTO 2340
2310     IF CODE$="BB" THEN PRINT #2, USING "####.##  |"; BB(I,J);: GOTO 2340
2320     IF CODE$="HE" THEN PRINT #2, USING "#.###^^^^|"; HE(I,J);: GOTO 2340
2330     IF CODE$="HD" THEN PRINT #2, USING "#.###^^^^|"; HD(I,J);: GOTO 2340
2340   NEXT J
2350   PRINT #2, " "
2360   IF I=COMP THEN PRINT #2,
"|_____|_____|_____|_____|_____|_____|_____|_____|_____|____
___|_____|_____|"
2370 NEXT I
2380 PRINT #2, " ":PRINT #2, " "
2390 RETURN
2400 '
2410 'SUBROUTINE:  PRINT HEADINGS ON THE COMPOSITION TABLES
2420 '
2430  PRINT #2, "

2440  PRINT #2, "|       |";
2450 FOR J=1 TO CLASS+1
2460  PRINT #2, "        |";
2470 NEXT J
2480 PRINT #2, " "
2490 PRINT #2, "|        |";
2500 FOR J=1 TO CLASS
2510  PRINT #2, USING "  ###  |";J;
2520 NEXT J
2530 PRINT #2, " TOTAL |"
2540 PRINT #2, "|        |";
2550 FOR J=1 TO CLASS +1
2560  PRINT #2, "        |";
2570 NEXT J
```

```
2580 PRINT #2, " "
2590  FOR I=6 TO COMP
2600   PRINT #2, USING "|#####";I;
2610   PRINT #2, "   |";
2620   FOR J=1 TO CLASS+1
2630     IF CODE$="Z" THEN PRINT #2, USING "####.###|"; Z(I,J);: GOTO 2670
2640     IF CODE$="ZW" THEN PRINT #2, USING "####.###|"; ZW(I,J);: GOTO 2670
2650     IF CODE$="ZF" THEN PRINT #2, USING "####.###|"; ZF(I,J);: GOTO 2670
2660     IF CODE$="ZL" THEN PRINT #2, USING "####.###|"; ZL(I,J);: GOTO 2670
2670   NEXT J
2680   PRINT #2, " "
2690   IF I=COMP THEN PRINT #2,
"|_____|_____|_____|_____|_____|_____|_____|_____|_____|__
____|_____|_____|
2700  NEXT I
2710  PRINT #2, "| TOTAL  |";
2720  I=COMP+1
2730   FOR J=1 TO CLASS+1
2740     IF CODE$="Z" THEN PRINT #2, USING "####.###|"; Z(I,J);: GOTO 2780
2750     IF CODE$="ZW" THEN PRINT #2, USING "####.###|"; ZW(I,J);: GOTO 2780
2760     IF CODE$="ZF" THEN PRINT #2, USING "####.###|"; ZF(I,J);: GOTO 2780
2770     IF CODE$="ZL" THEN PRINT #2, USING "####.###|"; ZL(I,J);: GOTO 2780
2780   NEXT J
2790   PRINT #2, " "
2800   PRINT #2,
"|_____|_____|_____|_____|_____|_____|_____|_____|_____|__
____|_____|_____|"
2810   PRINT #2, " ":PRINT #2, " "
2820 RETURN
2830 END


SYNTHETIC OIL
6,0.0,0.0,0.0,0.0,0.0,0.0,0.0,0.0,0.0,0.0
7,0.0,4.0,0.0,0.0,0.0,0.0,0.0,0.0,0.0,0.0
8,6.0,0.0,12.0,0.0,0.0,0.0,0.0,0.0,0.0,0.0
9,5.5,0.0,0.0,0.0,0.0,0.0,0.0,0.0,0.0,0.0
10,5.1,0.0,0.0,7.0,0.0,0.0,0.0,0.0,0.0,0.0
11,1.0,0.0,0.0,0.0,0.0,0.0,0.0,0.0,0.0,0.0
12,0.0,0.0,0.0,0.0,0.0,0.0,0.0,0.0,0.0,0.0
13,0.0,2.0,0.0,0.0,0.0,4.0,0.0,0.0,0.0,0.0
14,0.0,6.0,0.0,0.0,0.0,14.0,0.0,0.0,0.0,0.0
15,0.0,0.0,0.0,0.0,0.0,0.0,0.0,0.0,0.0,0.0
16,0.0,0.0,2.0,0.0,0.0,0.0,0.0,19.9,0.0,0.0
17,0.0,0.0,0.0,0.0,0.0,0.0,0.0,0.0,0.0,0.0
18,0.0,0.0,0.0,0.0,0.0,0.0,0.0,4.0,2.0,0.0
19,0.0,0.0,0.0,2.0,0.0,0.0,0.0,0.0,0.0,0.0
20,0.0,0.0,0.0,0.0,0.0,0.0,0.0,0.0,0.0,2.0
21,0.0,0.0,0.0,1.5,0.0,0.0,0.0,0.0,0.0,0.0
```

Figure C.2 Gas chromatograms of fresh Bunker C fuel oil and its saturate and aromatic fractions.

Fresh
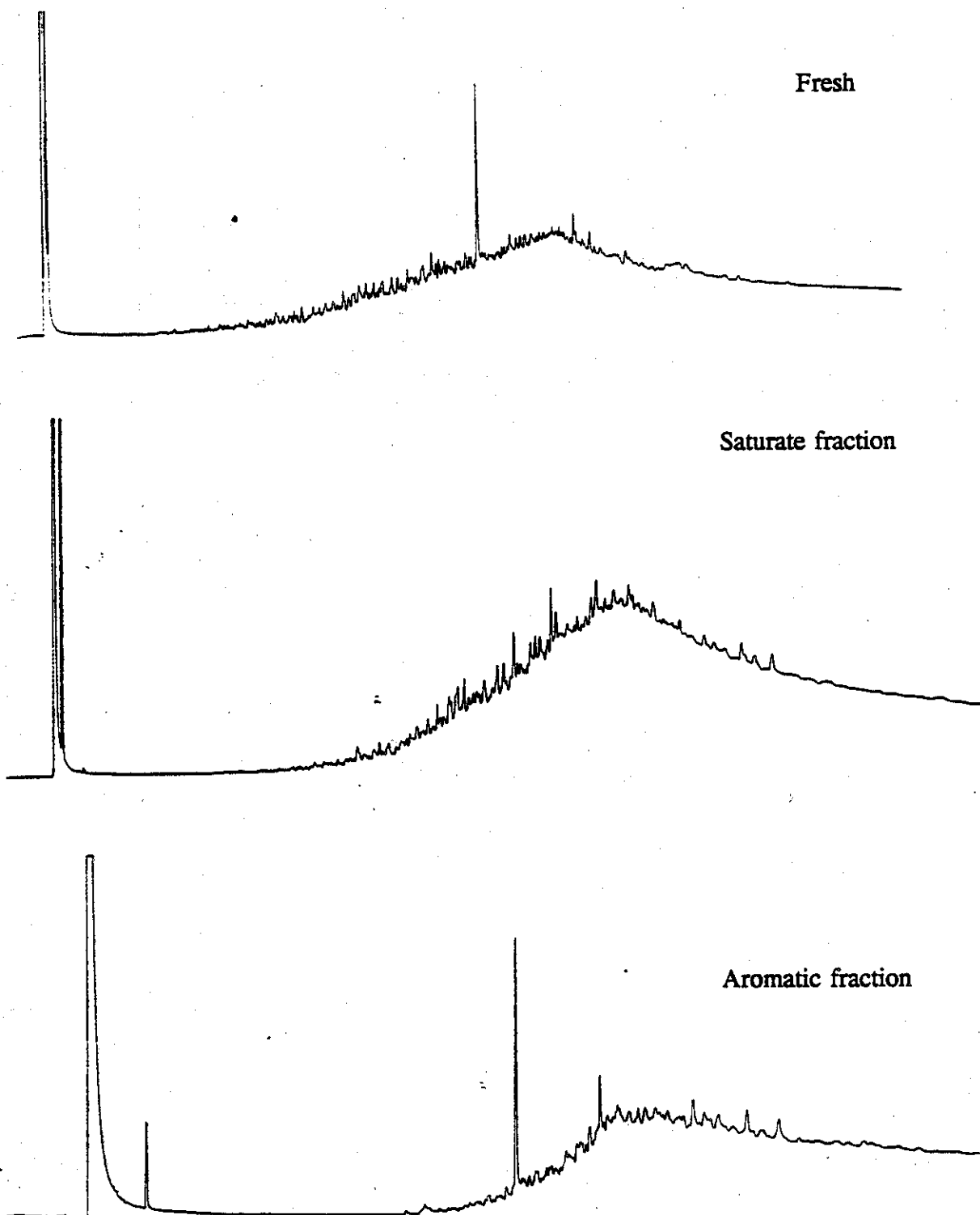
Saturate fraction

Aromatic fraction

Figure C.3 Gas chromatograms of Cold Lake Bitumen and its saturate and aromatic fractions.

APPENDIX D

Composition Matrices of Heavy Crude Oils

Table D.1 Matrix for initial mass per 100 g of California Crude API 15 oil or percent using the "Hydrocarbon class" approach

elution group	normal alkanes	branched alkanes	aromatics	polars	total
C_6	0.428	0.350	0.000	0.000	0.778
C_7	0.771	0.423	0.000	0.000	1.194
C_8	0.717	2.467	0.000	0.000	3.184
C_9	1.008	5.905	0.000	0.000	6.913
C_{10}	1.075	5.742	0.000	0.000	6.817
C_{11}	1.044	4.275	0.000	0.000	5.319
C_{12}	0.990	1.416	0.000	0.510	2.916
C_{13}	0.917	4.484	0.616	0.510	6.527
C_{14}	1.275	1.960	1.676	0.510	5.421
C_{15}	0.900	0.992	2.317	0.510	4.719
C_{16}	1.284	3.168	7.247	0.510	12.209
C_{17}	0.600	1.268	3.023	0.510	5.401
C_{18}	0.500	2.666	4.691	0.510	8.367
C_{19}	0.325	1.040	1.815	0.510	3.690
C_{20}	0.298	0.000	0.000	0.510	0.808
C_{21}	0.012	0.000	25.215	0.510	25.737
total	12.144	36.156	46.600	5.100	100.000

Table D.2 Matrix for initial mass per 100 g of California Crude API 11 oil or percent using the "Hydrocarbon class" approach

elution group	normal alkanes	branched alkanes	aromatics	polars	total
C_6	0.000	0.000	0.000	0.000	0.000
C_7	0.080	0.000	0.000	0.000	0.080
C_8	0.324	0.542	0.000	0.000	0.866
C_9	0.381	0.713	0.000	0.000	1.094
C_{10}	0.232	1.121	0.000	0.000	1.353
C_{11}	0.155	1.264	0.000	0.000	1.419
C_{12}	0.353	1.691	0.830	0.510	3.384
C_{13}	0.453	2.330	1.818	0.510	5.111
C_{14}	0.413	2.210	3.564	0.510	6.697
C_{15}	0.240	1.429	4.403	0.510	6.582
C_{16}	0.315	3.224	12.381	0.510	16.430
C_{17}	0.504	0.583	3.871	0.510	5.468
C_{18}	0.381	1.019	6.339	0.510	8.249
C_{19}	0.287	1.563	7.541	0.510	9.901
C_{20}	0.052	0.392	4.365	0.510	5.319
C_{21}	0.000	0.249	27.288	0.510	28.047
total	4.170	18.330	72.400	5.100	100.000

Table D.3 Matrix for initial mass per 100 g of Bunker C fuel oil or percent using the "Hydrocarbon class" approach

elution group	normal alkanes	branched alkanes	aromatics	polars	total
C_6	0.000	0.000	0.000	0.000	0.000
C_7	0.000	0.000	0.000	0.000	0.000
C_8	0.000	0.000	0.000	0.000	0.000
C_9	0.000	0.000	0.000	0.000	0.000
C_{10}	0.000	0.274	0.000	0.000	0.274
C_{11}	0.260	0.906	0.320	0.000	1.486
C_{12}	0.417	0.000	1.715	0.510	2.642
C_{13}	0.509	0.261	0.551	0.510	1.831
C_{14}	0.619	0.601	3.613	0.510	5.343
C_{15}	0.802	1.532	5.584	0.510	8.428
C_{16}	1.124	6.949	6.172	0.510	14.755
C_{17}	1.524	4.042	9.906	0.510	15.982
C_{18}	0.613	5.852	10.417	0.510	17.392
C_{19}	1.174	0.316	6.532	0.510	8.532
C_{20}	1.029	1.908	3.472	0.510	6.919
C_{21}	2.489	0.000	13.417	0.510	16.416
total	10.560	22.641	61.699	5.100	100.000